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E. Arthur Bearder.
H. T. Calvert, M.B.E., D.Sc., Ph.D., F.I.C.
J. W. Cobb, C.B.E., B.Sc., F.I.C.
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Morris W. Travers, D.Sc., F.R.S.
G. Weyman, D.Sc.
D. Woodroffe, M.Sc., A.I.C.

Editor :

T. F. Burton.

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REPORTS

OF THE

PROGRESS OF APPLIED CHEMISTRY.

PLANT AND MACHINERY.

By W. H. COLEMAN, F.I.C.,
Chemical Engineer, Glasgow.

THE year 1922 suffered from very considerable industrial depression, as did 1921, and this is probably the reason why it has been a comparatively poor year in new developments of chemical plant and machinery.

The great advances made during the war years and immediately after were, no doubt, in a large part due to the increased output of chemicals and allied products which was called for and the consequent working of all plant at its fullest capacity. From this intensive working it resulted that defects in design and construction, and in adaptation to the end in view, were very forcibly impressed on both the work's manager and the engineer as well as upon the owner and fostered the spirit of invention of new, and improvement of existing, plant, and, as there was plenty of money available, little hindrance was felt from this cause.

Taking the foregoing remarks into consideration, it is not to be wondered at that the past year has been so little remarkable for new ideas about plant. At the same time a good deal of steady progress has been made, especially in details.

Perhaps the most outstanding advance during the year has been the development of machinery for what may be described as extremely fine grinding. The advances made in colloid chemistry have focussed much attention upon the enormous influence which specific surface has upon the properties of solids and liquids. The chemical and electrical methods of dispersion are not very suitable for large-scale or manufacturing work, and a considerable amount of attention has been devoted to effecting the disintegration or dispersion of solids and liquids by mechanical attrition. Among the many machines put forward for this purpose the Plauson colloid mill is perhaps the most interesting; this machine was referred to last year, but considerable developments have since taken place, and it is now being made in this country and is available for use. It is necessary when grinding or disintegrating to produce a product of a fineness comparable with that of ultra-microscopic particles, that the operation should be conducted in a liquid medium, consequently the material to be dispersed is mixed with a suitable liquid—either water or an oil—and the mixture is passed through the mill, a full description of which has been given in the *Journal.*[1] The beaters are rotated at from 1000 to 3000 r.p.m., and the liquid carrying the solid particles with it is thrown or driven against the anvils at a speed of something like 2000 to 3000 metres per minute.

Another mill having the same object in view is the "Premier"; in this case the liquid carrying the solid to be dispersed is forced by means of a pump through an extremely narrow annular space formed between the bevelled edge of a circular opening in a fixed horizontal plate, and the bevelled edge of a horizontal disc which is rotated within the circular opening at a very high speed, with the result that the solid particles are torn apart into minute fragments. The clearance between the edge of the disc and that of the circular opening is capable of very fine adjustment by a micronometer screw, and the speed of the disc can be varied as required, so that particles of varying degrees of fineness are obtainable. Both of the above machines are said to take comparatively little power, and to be capable of producing satisfactory products. They are applicable to many departments of chemical industry, such as emulsifying fats, oils, waxes, etc., mixing paints, preparing the so-called soluble creosote disinfectants, preparing polishing pastes, making emulsions of tar, tar oils, bitumen and water for dust prevention and road binding, regenerating milk from milk powder, and for washing oils.

Although it is perhaps straining somewhat, the strict meaning of the terms plant and machinery, to include a notice of a material like "silica gel," yet, as its action is purely physical, and as it can in most cases be used over and over again, some mention of this interesting substance may be made. Silica gel is the trade name given to a form of silica prepared according to an American patent, and which is highly porous and possesses very strongly-marked adsorbent properties. It can be used for absorbing moisture and other vapours such as ether, acetone, benzene, etc., from mixtures with air or other gases, in which they occur in very small proportions, enabling them to be recovered in a practically pure condition by subsequently heating the saturated gel. Sulphur dioxide is also absorbed from gaseous mixtures, in which it occurs in very small proportion, as for instance, smelter smoke, and the sulphur dioxide is regained by heating the saturated gel. It has been applied to the recovery and refining of petroleum oils, and forms a very efficient substratum or support for catalytic materials.

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[1] *J.*, 1922, 435R.

Another substance which may also be referred to here is "bentonite," a peculiar kind of clay found in Wyoming and California in the United States and in some parts of Canada. The special properties which distinguish this clay are its ability to absorb nearly three times its weight of water, and its very great adsorptive power for colouring matters. It is this last property which is of interest in chemical industry, as it has been successfully applied to the de-inking of newsprint.

The utilisation of the water resources of the country has occupied the attention of the authorities for some time, and the publication of the Final Report of the Water Power Resources Committee[2] is of considerable interest. It is estimated that over 200,000 kw. continuous output could be obtained at an economic rate from certain undeveloped resources in Great Britain, chiefly in the Scottish Highlands, this is equal to about 40% of the power station output of Great Britain for the year 1917–1918, and if this were utilised it would enable a saving of some 3,000,000 tons of coal per year to be made. The Committee recommends that a Water Commission should be set up to obtain further data on the question, and also to investigate the possibilities of utilising the power of the tides.

In connexion with the foregoing, the paper on the Generation of Steam by Electricity, read at Montreal by F. T. Kaelin, chief engineer to the Shawinigan Water and Power Co.,[3] is of great interest. Particulars are given of a plant in which the water itself formed the resistance, and it is stated that the manipulation of a properly installed system is simple and safe, that the equipment is inexpensive and requires very little space in comparison with its capacity.

Practical experience had shown that an efficiency of 98% net could be obtained, and that 1 kw.-hour was equal to about 3·12 lb. of steam. The importance of these figures lies in the fact that if the water power of the Highlands is to be used for chemical manufactures the way is now clear in which the steam, without which very few chemical industries can be carried on, may be obtained with a comparatively simple plant, and at a reasonable outlay, without having to carry coal to districts which are not too easily reached from even the nearest coal fields.

The heating and cooling of all kinds of materials forms an almost inseparable part of most processes of chemical industry. Up to recent times, whenever a temperature above 100° C. has been required, high-pressure steam or direct fire has been used with the consequent risks of explosion and fire if the materials undergoing treatment were of an inflammable nature. The method which is taking the place of these systems is that of heating indirectly, by means of an oil of high flash and boiling points.

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[2] *J.*, 1922, 63R.

[3] *J.*, 1922, 94R, 412R.

In the Merrill system of indirect heating a suitable petroleum oil is used as the medium; the system consists of a furnace provided with a coil in which the oil is heated, a pump by which the oil is circulated, and a coil of pipe arranged in a suitable manner in the vessel that contains the material to be heated. These three parts are connected together by a piping system in which is included an expansion vessel, open to the atmosphere, so that no great increase of pressure can occur. The furnace may, if desired, be placed in another building so as to be completely isolated from the vessel which contains the material to be heated, thus avoiding all risks of fire. Any difference of temperature that is desired may be maintained between the circulating oil and the material being heated so that the rate of heating is under perfect control. Any temperature up to about 315° C. can be obtained with the oils now in use, and the system is particularly suited for such operations as gum running, varnish making, and distilling inflammable liquids.

Mercury vapour has been proposed as a heat-carrying medium,[4] but the high cost and its poisonous properties would seem to be rather against its extensive use.

A somewhat novel method of heating various materials, but chiefly applied to distilling tar and to cracking oils, consists in forcing the tar or other material below the surface of molten lead or other suitable metal kept at the desired temperature. The portion which is vapourised is passed on to a condenser, or to another vessel for treatment, and the non-volatile portion is removed from the surface of the molten metal, either flowing away through a trap if it is liquid, or if solid or viscous, being removed by a scraper.[5]

A good number of patents have been taken out for improvements in furnaces of all kinds, chiefly concerned with details of structure, flues and regenerators, etc. These do not call for any particular notice, but mention should perhaps be made of the "Fusion patent rotary retort."[6]

It consists of an outer horizontal tube, rotated on rollers, with an inner coaxial tube, and provided with special gas-tight connexions at the ends. A shaft passes eccentrically through the tube, and a number of hammers are suspended from the shaft so that as the tube rotates the hammer heads are carried some little way round the periphery, and at last fall back to the lowest position, and in so doing they strike a glancing blow upon anything in their path, keeping the tube free from scale and deposits of all kinds, as well as breaking up the material being treated, and preventing it fritting together. The outer tube is heated externally, and the material passes first through the inner tube and then through the annular space between the tubes. The furnace is intended primarily for retorting shale and coal, but should be applicable to other uses.

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[4] U.S.P. 1,403,471; *J.*, 1922, 164A.
[5] E.P. 174,690; *J.*, 1922, 205A.
[6] *J.*, 1922, 580A.

Cooling and refrigerating machinery has received the usual amount of attention, to judge from the patent literature. The chief new idea to be noticed is the claim by R. Plank,[7] in a paper on the efficiency of compression refrigerating machines, that he can get an increase of 18% in cooling efficiency at the cost of an increase of only 7% in power consumption, by further compressing and again cooling the previously compressed and cooled gas or condensed liquid medium. We are not told what is the extra expenditure of capital, upkeep, cooling water, etc.—points so often omitted by the inventor, but which the manufacturer must consider most carefully if he is to make a profit.

Heat insulators are, or should be, of very great interest to the chemical manufacturer, the waste of heat in many of the smaller factories being often very great, not only by loss by radiation from hot surfaces, but also by leakage of heat into vessels and chambers which are required to be maintained at low temperatures. Two materials are referred to in a paper by E. Griffiths and J. H. Awbery,[8] read before the Faraday Society. One is "expanded rubber," or rubber in a highly cellular form, with a density of only 0·06 (ordinary vulcanised rubber has a density of 1·5), the other is Balsa wood from Ecuador, a cubic foot of which weighs only from 5·7 to 8·6 lb., against 45 lb. for mahogany ; it has also the further advantage that, although it has little strength, it can be worked with ordinary woodworking tools, which is not the case with cork.

Among the smaller pieces of apparatus that are likely to be serviceable to manufacturers may be noted the very useful and portable dew point hygrometer, described by J. W. Hinchley at the Society's Annual Meeting,[9] and the useful piece of apparatus for rapidly calibrating the capacity of storage and other vessels, described at the same meeting by J. W. McDavid.[10] The latter apparatus, which weighs complete only about 26 lb., and is consequently very portable, consists of a small vessel on a stand, which can be kept full of water to a constant level by means of an overflow, and which has an outlet provided with a nozzle of definite aperture.

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[7] *Z. ges. Kälteind.*, 1921, **28**, 157 ; *J.*, 1922, 489A.

[8] *J.*, 1922, 474R.

[9] *J.*, 1922, 242T.

[10] *J.*, 1922, 295T.

The time of outflow of a definite quantity of liquid from a particular nozzle having been determined, the calibration of the tank is effected by noting the time taken to fill it to various levels. From the results of a number of observations a curve can be constructed.

The application of the process of froth flotation has been extended, and having been applied to the treatment of coal to improve its coking properties, it is now proposed to apply the process to the treatment of " caliche " for the recovery of sodium nitrate.

The production of fair-sized individual crystals instead of very small ones or crystalline masses is receiving more attention. The growing of sugar crystals in the vacuum pan (graining) has long been known, but it is only recently that the idea has been applied to chemical products generally. A saturated solution of the pure salt is caused to flow slowly through a very long trough filled with small crystals, which are kept in constant motion, or rather, agitation, by giving the trough an oscillating motion. Under these conditions the crystals increase in size without adhering to one another, and a product is obtained which has not only a nice appearance, but which is free from inclusions of mother liquor, and consequently very pure.

Foams formed from solutions containing glue, gelatin, glucose, and some hardening agent by means of an inert gas, such as carbon dioxide, have been used for some time for extinguishing fires in oil tanks etc. ; they are now being tried to prevent loss of volatile liquids from storage vessels with, it is claimed, very satisfactory results. A note may be made here of the warning issued by the U.S.A. Bureau of Mines against the use of carbon tetrachloride as a fire-extinguishing agent. They find that very much phosgene at a dangerous concentration is liable to be formed, especially in enclosed premises.

Some additions to our knowledge of materials for the construction of plant of various kinds have been made during the year. A. F. Greaves-Walker finds[11] that sillimanite, a stable aluminium silicate, remains rigid on heating, and can be used safely up to within a few degrees of its melting point. It has a constant volume at high temperature, and a low co-efficient of expansion, and consequently, does not spall easily. It is neutral in reaction, and if burned at a sufficiently high temperature, it is impervious to slags and metals.

Basalt, which has a high resistance to acids, can be melted at about 1300° C. without losing this property, and can then be cast into moulds to form vessels and tanks, which can be strengthened mechanically by inserting iron reinforcing rods into the molten stone.[12]

When and where wood can be obtained at a reasonable price it offers certain advantages as a material for the construction of chemical plant, especially for tanks, vats, and pipes. It is not liable to electrolysis, as is frequently the case with metal pipes, it is a poor conductor of heat, and withstands weak acid solutions quite well. Some very interesting data about the properties of wood and ideas for the construction of wooden chemical plant of various kinds will be found in a paper by C. S. Robinson.[13]

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[11] J., 1922, 43T.
[12] J., 1922, 263R.

Anyone who has trouble with corrosion of pipes will find much useful matter in the paper by J. W. Shipley,[14] which, although concerned with the corrosion of iron and lead pipes in certain alkaline soils in Canada, contains a good deal of matter which is of general interest on the question of corrosion.

" Stainless steel," or high chromium steel, if it were not so expensive, should be of considerable use in the construction of chemical plant, as it withstands the action of caustic liquors, ammonia, copper sulphate, and nitric acid. Strange to say, it is attacked by acetic, citric, lactic, and tannic acids, but withstands vinegar, lemon juice, sour milk, and tannin extracts which contain these acids.[15] Stainless steel has its resistance to corrosion increased by hardening, and it withstands high temperatures without excessive loss of strength.

The process of forming a skin or alloy of aluminium on the surface of iron, steel and other metals known as " calorising," is claimed to protect the metal against the oxidising action of flue gases at temperatures up to nearly 1000° C., and should find many applications.

The useful work of the British Association of Chemical Plant Manufacturers has been continued, and they have issued a report on the standardisation of jacketed pans, and on the applicability of nickel for use in the construction of chemical plant.[16]

A good deal of very useful work has been carried out by various investigators, which will be helpful to all those who have to design, construct, or use many kinds of plant. The list of references which follows will be of interest. It would seem to be desirable that some authoritative body should undertake collection of data of this kind, and carefully sort it out, rejecting anything that is not satisfactory. All that is of value should be made available for reference under the proper headings, and the gaps indicated so that research might proceed on useful lines and a great deal of duplication of work avoided.

Work on the following subjects has appeared during the year :— Researches on heat transference (W. H. McAdams and T. H.

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[13] *J. Ind. Eng. Chem.*, 1922, **14**, 607 ; *J.*, 1922, 619A.

[14] *J.*, 1922, 311T.

[15] *Chem. and Met. Eng.*, 1922, **27**, 532.

[16] *J.*, 1922, 52R.

Frost,[17] F. R. Bichowsky,[18] and W. G. Whitman and J. L. Keats[19]) the control of industrial heating processes (J. A. Doyle[20]), the efficiency of steam pipe coverings (C. Jakeman[21]), volume of air required for drying (C. T. Mitchell[22]), the boiling points of salt solutions (E. M. Baker and V. H. Waite[23]), the general problem of evaporation (J. W. Hinchley[24]), the evaporation of a liquid into a gas (W. K. Lewis[25]), distillation and rectification (L. Gay[26]), relation between the composition of vapour and liquid in distilling columns (E. Piron[27]), vapour pressures, heats of vaporisation and curves from which theoretical columns may be designed, and their efficiencies calculated (W. K. Lewis and H. C. Weber[28]), efficiency of fractionating columns (W. A. Peters, jun.[29]), tar distillation (W. A. Walmsley[30]), design and working of ammoniacal liquor stills (P. Parrish[31]). Reference only has been made to above work, as it would be impossible to do more than pick out points here and there, but anyone who is in any way interested in any of the subjects should refer to the original publications.

[17] *J. Ind. Eng. Chem.*, 1922, **14**, 13; *J.*, 1922, 279A.

[18] *Ibid.*, 1922, **14**, 62.

[19] *Ibid.*, 1922, **14**, 186; *J.*, 1922, 315A.

[20] *Ibid.*, 1922, **14**, 1005.

[21] *Engineering*, 1922, **114**, 155; *J.*, 1922, 697A.

[22] *Chem. and Met. Eng.*, 1921, **25**, 1088; *J.*, 1922, 43A.

[23] Amer. Inst. Chem. Eng.; *J.*, 1922, 87A.

[24] *J.*, 1922, 242T.

[25] *Chem. and Met. Eng.*, 1922, **27**, 112; *J.*, 1922, 885A.

[26] *Chim. et Ind.*, 1921, **6**, 567; *J.*, 1922, 43A.

[27] *Chem. and Met. Eng.*, 1922, **26**, 317; *J.*, 1922, 239A.

[28] *J. Ind. Eng. Chem.*, 1922, **14**, 485; *J.*, 1922, 573A.

[29] *Ibid.*, 1922, **14**, 476; *J.*, 1922, 619A.

[30] *J.*, 1922, 296T.

[31] *J.*, 1922, 229T.

FUEL.

By JOHN W. COBB, C.B.E., B.Sc., F.I.C., and H. J. HODSMAN, M.B.E., M.Sc., F.I.C.,

Department of Coal Gas and Fuel Industries, The University, Leeds.

THE revived interest in all fuel problems which has characterised the post-war period is further indicated by the recent developments of periodical literature specially devoted to fuel. Last year saw the launching of the journal *Brennstoff-Chemie*, under the direction of F. Fischer of the Coal Research Institute at Mulheim. This journal, as its name implies, is essentially chemical in scope. In France a new journal, *Chaleur et Industrie*, has appeared. The current year has seen the appearance of a monthly supplement of the *Colliery Guardian—Fuel in Science and Practice*, under the editorship of Professor R. V. Wheeler, of Sheffield. This periodical contains articles, mainly on current topics of the science of coal, reviews of current literature and patent applications, and a bibliography, although neither here nor elsewhere does this last receive adequate treatment. The Federation of British Industries, which has given encouragement to fuel economy in industrial practice, issues a quarterly periodical, *Fuel Economy*, dealing mainly with descriptions of modern fuel plant and efficient practice.

The appearance of this periodical literature is evidence of an increased interest in fuel questions. The multiplication of journals is not without its embarrassment for those who, for any reason, feel bound to read them all, but is undoubtedly leading to the diffusion of much useful and interesting technical information. It lessens the probability of work going unpublished, although perhaps it increases the danger of even good work going unread.

At the outset some reference should be made to the great fall in the value of coal and other fuels, which has occurred in the last eighteen months or so, for this has an important bearing on many technical questions. The price of liquid fuel, however, has shown a still more marked fall than that of coal, and this naturally affects the finances of carbonising industries. The circumstances of the coal industry have been widely debated in the public press, and need no reiteration here. The revival of the coal export trade, and of some industries in the summer of 1922, has caused some increase in prices, and the price of coal shows no further tendency to revert to pre-war values.

SMOKE ABATEMENT.

It must be borne in mind that the British fuel problem, in the main, is to make the best of bituminous coals, which constitute the bulk of our supplies, judged by a threefold standard of thermal efficiency, chemical efficiency and the absence of atmospheric pollution. The year 1922 has seen the publication of the Government Committee's final report[1] on "Smoke Abatement," and action based upon it has been initiated. Public opinion is becoming gradually aroused to the desirability of smoke abatement. It is plain that any insistence on smokeless combustion would have a far-reaching effect on fuel technology, and much of the scientific and technical work on fuel problems is inspired by the recognised necessity for it.

One of the most striking conclusions of the report is that, speaking broadly, our smoke nuisance is essentially of domestic origin. Comparing domestic and industrial smoke, the former, though diluted and diffused, is found to be quantitatively more important, and qualitatively more harmful, owing to its tarry character, which renders it more adherent. Industrial smoke, owing to the higher temperature of the furnaces producing it, is often to all intents simply carbon and grit. Being produced in large units it is locally more concentrated and obvious to the eye. The evidence, which is more likely to appeal to chemists, is partly based on analyses of town soot, and also on meteorological observations of an independent character. It points to the conclusion that something like three-fourths of the total smoke is made by the household fire. There is, moreover, a marked tendency towards the elimination of much industrial smoke in consequence of the attention paid to economy of fuel, and the development of public power supply systems should tend in the same direction if the power stations are properly equipped and staffed. The report recommended some tightening up of the control of industrial smoke, the prohibition of smoky fireplaces in new public buildings, and the limitation of smoky fireplaces in new dwelling houses, especially where built with the assistance of public funds.

The late Government took some action on this report by introducing a bill before Parliament, though there are signs that it will prove abortive. The bill is much more timid than the report, and is, apparently, mainly directed to more rigorous control of industrial chimneys. If the conclusions of the various investigators are valid, this will leave matters much as they were.

A small book, "The Smokeless City," by E. D. Simon and M. Fitzgerald (Longmans), contains a readable account of the findings of the Smoke Abatement Committee, and also the authors' view of the steps which are desirable and practicable for dealing with the domestic smoke nuisance.

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[1] *J.*, 1922, Jr.

DOMESTIC AND SMOKELESS FUELS.

The individual—especially the small householder—is largely helpless, having little or no option as to the choice of appliances and fuel. Until recently no one could confidently advise him, owing to the absence of any sure information as to the comparative *performances of fuels or fires. This lack is, however, being rapidly* dispelled.

Mrs. M. W. Fishenden[2] has amplified her investigations on domestic fireplaces.[3] The open firegrates previously used were again examined when burning cakes of coke prepared by carbonising coal at low temperatures at the Fuel Research Station, Greenwich. The proportion of the heat of combustion of the fuel which was radiated was found to be some 25% greater when the coke cakes were burned than when raw coal was used. The measurements were extended to kitchen fireplaces with back boilers, three of which were tested, one being of old-fashioned and primitive pattern. It is interesting to note that one experience previously reported with the ordinary grates was repeated here. The new designs tested were not necessarily thermally more efficient as regards water-heating and radiation than the old, but their smaller fuel-using capacity made it more difficult to burn fuel to waste in them. The ordinary kitchen range—intended to perform at least a three-fold function, of heating water, cooking, and room-warming—did no one in a thermally efficient manner. The radiant efficiency with coal firing was only about 10% as against 20–25% in the simple firegrate with no attachments. The corresponding boiler efficiencies were 13–17%, suggesting that the heat utilised in the water boiler had been obtained mainly at the expense of that otherwise radiated into the room. When fired with the coke cakes the corresponding figures were 14·5–20·7%. In striking contrast were the results obtained in an independent boiler with visible fire burning the coke cakes, when water was heated with an efficiency of 42%. Combined with gas for cooking it was considered that such a boiler might replace the old kitchen range without proving more costly, and also without the production of smoke. It will be seen that coke, whether of high-temperature or low-temperature origin, showed some thermal superiority over coal in ranges of standard pattern, and could be used with very much greater advantage in appliances designed for this purpose.

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[2] *Fuel Research Board Tech. Paper No.* 3; *J.*, 1922, 13R.
[3] See *Fifth Rept.*, p. 28.

The results of the tests on kitchen ranges receive general confirmation in the tests on ranges and cooking appliances by A. H. Barker.[4] The evaluation of the utility of a kitchen range designed to serve several purposes simultaneously is difficult. There are so many ways of using the appliance according to the needs or caprice of the user. Variation in design and scope of different appliances adds to the difficulties of comparison. Moreover, the definition of efficiency for cooking purposes presents very serious obstacles. Nevertheless, Barker has dealt copiously and courageously with the problem and in particular with the efficiency of ovens, measuring the heat transmitted to a coil carrying water placed inside the oven, and determining an efficiency as arbitrarily defined.

The thermal efficiencies of the ovens studied ranged from 1 to 5% with an average of 2½%. The efficiency of the boilers attached to the ranges was 11–12% in the majority of ranges tested, although in one case the figure reached 20%. The hot-plate efficiencies were 1–5%. Considering the apparatus as a whole, the total amount of heat regarded as usefully employed when all the apparatus was simultaneously in use for cooking purposes was calculated in each case against the total heat of the fuel consumed. The efficiency, which naturally varied with the fuel consumption, varied from 5 to 11%, and in most cases was about 7%. At the same time, it should be noted, Barker showed that these figures could be largely exceeded by the use of solid fuel ranges of special design.

It can with some reason be urged that these physical tests do not necessarily give an index of the service rendered in practice. Therefore a set of tests was carried out in which a certain menu was cooked on the range with a corresponding production of hot water, and special interest attaches to these tests because they were also made on gas cookers as in ordinary use. The thermal efficiencies of the ovens of the two coal-fired ranges were determined as 5·5 and 5·8% respectively, while that of a gas cooker of standard type reached 38%, and the latter showed a financial advantage. The thermal efficiency of the gas cooker for total heating work done was also greater than those of the coal-fired ranges, but financially the gas was more costly. This was due to the expense of heating water on the gas cooker hot plate. Barker concludes that if the hot water were provided by a separate economical water heater, the use of gaseous fuel might become as cheap as or even cheaper than the use of coal, although such a conclusion as applied to general domestic use is difficult to draw from special laboratory experiments.

If prominence is given here to the domestic fuel problem, it is not without good reason. We have seen its importance as regards atmospheric pollution. The coal used as domestic fuel is one of the largest single items in the national fuel bill, and it commands the highest price in the coal market. The manufacture of good solid domestic fuel obviously offers great scope, and it is not surprising that investigators of solid smokeless fuels seek first to meet the requirements of domestic consumption. If such a fuel cannot find a sale in this market it will be much more difficult to establish one against the lower-priced industrial fuel. Moreover, experience gained in meeting household requirements may be applied with advantage in other directions. Household fuels hold a key position in fuel technology, and much of the technical work on coals has been inspired by the problems which it presents.

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[4] *Fuel Research Board Special Report No. 4.*

The importance of the small householder's fireplace (the kitchen range) has been well recognised. It has been often assumed that a smokeless fuel adapted to such an appliance must necessarily be prepared by partially carbonising coal at a low temperature, so as to leave a portion of the volatile matter in the product. Such a process has to cope with difficulties in practice so serious that, after many years of effort, no large stable industry has as yet been established. The friability of the coke makes its transportation difficult; the low yield of gas, whether measured by volume or heat, and of ammonia, renders the process unattractive to gas manufacturers. The tar, though large in quantity, is of abnormal composition and of unproved value, except as a liquid fuel; it is deficient in aromatic hydrocarbons, but contains an abnormal proportion of tar acids. Such a product has possibly great potentialities, but these are still largely unknown. The existing coal-tar industry has developed only slowly, and as its chemistry has become more fully understood. The proper utilisation of low-temperature tar may demand the same prolonged chemical study.

The existing high-temperature carbonisation industries have stable markets for all their products, which suffice for the costs of manufacture and profits on capital. The town gasworks depend primarily on receiving a good price for the gas which pays the cost of carbonisation, and is only justified by the higher value in use of the thermal unit in gas as compared with coal. If the low-temperature coke industries fail to obtain a good return on their secondary products this leeway can only be made up either by evolving a much cheaper process of carbonisation or by obtaining a high price for the coke, and for this it will be necessary to show an efficiency in use considerably greater than that of coal. It seems very doubtful if the general consumer will voluntarily pay much more for any form of coke than for household coal for use in existing fireplaces, and in this the researches of Mrs. Fishenden give him support as long as he considers heating value alone.

This year has seen important contributions to the question which reveal it in a new and more hopeful light. The free-burning quality—combustibility—for which the low-temperature treatment was believed to be essential, is to be ascribed, according to E. R. Sutcliffe and E. C. Evans,[5] to the attainment of a suitable cell structure, given which, the temperature of carbonisation is relatively unimportant.

The results of H. D. Greenwood and J. W. Cobb[6] have a bearing on the subject. They showed that the true specific gravity of the product of carbonising a coal in the laboratory was greater when the carbonising temperature was 800° C., than when 500° C., *i.e.*, the material itself, apart from its pores, became denser, but that when the coal was carbonised at 1100° C. no higher specific gravity was found. The 1100° C. coke had a smaller percentage porosity than the 800° C. coke, and the cell walls were presumably thicker, which would explain a slower combustion without invoking any marked change in the chemical character of the coke material.

Of course, the difference between ordinary gas coke and the specially prepared products may be easily exaggerated. C. V. Boys[7] claims that ordinary coke can be burned without difficulty in an ordinary open grate if this is suitably arranged. The essential points are conservation of the temperature of the coke, as by eliminating ironwork and avoidance of the cooling effect of excess air by restricting the air supply.

Sutcliffe and Evans claim to have attained the right structure in the coke by a preliminary fine grinding of the coal—coking or non-coking—and subsequent briquetting, either with a binder, or better, by compression alone. Microscopical work by Sir George Beilby[8] adds support to the contention that the structure obtained is one of inter-connected fine pores similar to that of charcoal. Given this preliminary treatment, the production of free-burning smokeless fuel may be effected, it is claimed, in existing carbonising plant, and under existing conditions of operation, although the authors believe that in establishing new plant, special internally-heated retorts would be more economical. The process is free in important respects from the limitations which have prevented gas engineers from taking up the low-temperature carbonisation processes in the past. Moreover, where the gas industry does not develop in the direction of complete gasification it must find an outlet for the increased production of coke which accompanies its growing output of gas. The manufacture of a free-burning smokeless fuel for domestic purposes is one way of doing this, and some progress in this direction has been made by the South Metropolitan Gas Company.[9]

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[5] *J.*, 1922, 196T.
[6] *J.*, 1922, 181T.
[7] *Gas J.*, 1922, 157, 81
[8] *J.*, 1922, 341T.

Sutcliffe and Evans believe that if the manufacture of such a smokeless fuel can be established for domestic purposes, its superior "combustibility" will give it a place in industrial applications, such as steam raising for use in gas producers, and more particularly in blast-furnace practice.

It was recognised even by Sir Lowthian Bell that blast furnaces using charcoal can be worked with a smaller fuel consumption than the normal coke-fed furnace, and this is now ascribed to the superior "combustibility" of the charcoal. Sutcliffe and Evans believe that their coke would have similar properties, and a similar efficiency in the blast furnace. The importance of converting this belief into a demonstrable certainty is obvious. Time and experience will show how far these anticipations are realisable. Meanwhile this paper brings forward new ideas in the treatment of bituminous coal, emphasises the importance of the study of domestic fuel, and indicates its repercussion on other branches of fuel technology.

The development of these ideas will demand the use of more precise methods of measuring combustibility than those employed in the work referred to. It may be that some characteristic such as an "ignition temperature" determined under carefully specified conditions will suffice, and from time to time such methods have been worked out.[10] K. Bunte and A. Kölmel[11] have made similar measurements on cokes differing in mode of preparation. Their experience supports the claims made above. The ignition temperature of cokes measured depended on the kind rather than the percentage volume of pores, and in no discoverable way with the percentage of volatile matter. The ignition temperature of a low-temperature coke remained substantially the same when carbonisation was completed at 800° C. in an atmosphere of nitrogen. E. Erdmann,[12] in a comprehensive discussion of spontaneous combustion, rather with reference to lignites, has also described a method of measuring ignition temperatures.[13]

The importance of coke structure has given an increased importance to the determination of the specific gravity of such solids, which is beset with practical difficulties. Several papers dealing with this important matter have appeared recently.[14]

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[9] *Gas J.*, 1922, **157**, 375.

[10] *Cf.* Dennstedt and Schäper, *Z. angew. Chem.*, 1912, **25**, 2625 ; *J.*, 1913, 11 ; R. V. Wheeler, *Chem. Soc. Trans.*, 1918, **113**, 945 ; *J.*, 1919, 65A ; F. S. Sinnatt and B. Moore, *J.*, 1920, 72T.

[11] *Gas- u. Wasserfach*, 1922, **65**, 592; *J.*, 1923, 132A.

[12] *Brennstoff-Chem.*, 1922, **3**, 257, 278, 293 ; *J.*, 1922, 887A.

[13] *Cf.* also F. Plenz, *Gas u. Wasserfach*, 1922, **65**, 478 ; *J.*, 1922, 658A.

The Fuel Research Board's Report for 1922[15] is another important contribution to the subject of domestic fuel and low-temperature carbonisation. The prospects of low-temperature carbonisation are now discussed in the light of recent experience, both technical and economic. In the latter field a most important change is the fall in price of fuel oil from £15 to £4 per ton, involving a diminution of at least 10s. in the value of the products from one ton of coal. It becomes, then, the more necessary that all the other products shall find a remunerative and adequate outlet. It has been established that, in low-temperature carbonisation a gas of calorific value of, roundly, 1000 B.Th.U. per cub. ft. is producible, suitable for bringing lower-grade gas to a higher calorific standard by admixture. Applied for this purpose, under certain conditions, the gas might become the most valuable and least speculative of the assets of low-temperature carbonisation. It would also link up the process to the carbonising industries established for gas and coke manufacture.

As a result of the experience of the Research Station, it has been possible to establish standards of yield which are demonstrably attainable from suitable coal carbonised in externally-heated retorts, *viz.* :—Yields at 600° C., per ton of coal (dry) : Coke, 14·5–15·5 cwt. ; crude oil, 13·0–17·0 gal. ; liquor, 7·0–15·0 gal. ; ammonium sulphate, 4·5–8·5 lb. ; gas, 3000–3500 cub. ft. (25 to 35 therms).

In assessing the financial prospects of the process, it is assumed that the coke would command a figure which would pay for the coal treated. Then the crude oil, selling at 5d. per gallon, and the gas at 4d. per therm, would, for the above yields, bring in 16s. per ton of coal carbonised. This would have to bear the fixed and working charges and supply the profit on the enterprise. Success would plainly demand the evolution of carbonising apparatus which could be cheaply erected, maintained, and operated.

In the light of available experience, the question is asked : "Will it be possible to establish on sound industrial lines a new industry based on the carbonisation of tens of millions of tons of coal per annum now being consumed in the raw state ?" And the answer given is a conditional "Yes," "the elements of uncertainty being mainly economic and social."

The report contains an interesting study of the micro-structure of coke, which reinforces the conclusions of Sutcliffe and Evans (*loc. cit.*).

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[14] E. W. Washburn and others, *J. Amer. Ceram. Soc.*, **4**, 916, 961, 983 ; **5**, 48, 112. A. Schmolke, *Stahl u. Eisen*, 1922, **42**, 1237 ; **J.**, 1922, 798A. J. Gloetzer, *Brennstoff-Chem.*, 1922, **3**, 344 ; *J.*, 1923, 4A.

[15] *J.*, 1922, 270R.

Attention has been paid to the preliminary classification of coals by laboratory testing—a matter of fundamental importance. *Sometimes a coke is more and sometimes less bulky than the original coal. Coals of the former type cause difficulty in carbonisation* at low temperature, and may yield unsatisfactory products. Admixture with non-caking coal, or coke, in suitable proportions, prevents the development of this swelling, thus widening the field of raw materials available and affording a means of carbonising non-caking coals with recovery of their by-products. This "blending" of coals for carbonisation seems to offer possibilities to the existing high-temperature industries of gas and coke manufacture, and is not without its effect on the combustion of the coke produced. The laboratory assay method previously described[16] forms a convenient method of controlling the blending process.

The working experience of low-temperature carbonisation reported has been obtained in carbonising coal at 600° C. in externally-heated horizontal steel retorts of special construction. The charge of coal was placed in trays divided by partitions into square compartments so that the resulting coke was in the form of 6-inch square cakes which, when made from a suitable coal or blend, were easily removed and of good mechanical strength. The partitions assisted in conveying the necessary heat to the coal. There is a limit to the shortening of the coking period if a suitable product is to be obtained, for carbonisation, viewed as a chemical process, is a relatively slow reaction. For the production of these cakes, three hours' heating at 600° C. was necessary.

The liquid products, though greater in quantity than in standard high-temperature practice, are not without their shortcomings. The oils from the different coals tested were similar in nature. Most characteristic was the high proportion of tar acids, reaching in some fractions 50%. The crude oil was largely emulsified with liquor, but removal of suspended solids by filtration facilitated separation of the water by subsequent settling. The settled product had a calorific value of 16,000 to 16,500 B.Th.U. per lb. The flash point was too low for Admiralty purposes, and after removing light oil to correct this, the viscosity became excessive. It is believed that these conflicting requirements may be met after further study. The crude oil displayed another serious shortcoming. There was usually a limit to its miscibility with mineral fuel oils, and if this was overstepped, a gummy mass was deposited. The crude oil was completely immiscible with shale and American fuel oil, and only partially miscible with most of the others tried. Trinidad oil alone of those tested appeared to mix satisfactorily.

At a meeting of the South Wales Institute of Engineers on

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[16] *Fuel Research Board Tech. Rept.* No. 1; *J.*, 1921, 205A.

April 20th, there was an interesting and valuable symposium on low-temperature carbonisation by a number of workers in this field, new and old. The processes already mentioned and some others were described.

C. J. Goodwin[17] described the "Fusion" retort which is externally heated. The results given are for the treatment of oil shales. The retort is fitted with revolving breakers to prevent accretions on the inside of the retort, and if coal were treated the carbonised residue would need to be briquetted for most purposes.

H. Nielsen[18] proposes a revolving retort somewhat after the style of a cement furnace, but carbonises the coal by the sensible heat of producer-gas (L.M.N. process) which traverses the retort counter to the coal. The process can be worked for making low-temperature coke with the production of a mixed gas of moderate heating power, or the whole of the coke obtained can be gasified in the producer. It is stated that a plant for dealing with 100 tons of coal per day is being erected in India. In order to produce a mixed gas of somewhat higher grade, Nielsen also proposes the use of hot water-gas for the internal heating. The loss of heat in the "blow" gases is, however, very appreciable, and the suggestion is made that the working should be modified so as to produce, at the expense of the yield of water-gas, a "blow" gas containing such a proportion of carbon monoxide as to have a calorific value of about 110 B.Th.U. per cub. ft. It would then be good enough for heating or for use in gas engines for the production of power. This runs counter to normal water-gas practice which aims at minimising the heat content of the blow gas.[19]

S. R. Illingworth[20] has patented his method of fractional carbonisation in which it is arranged that the charge shall contain a suitable quantity and kind of volatile matter just as the plastic coke mass is setting.

Other types of plant and process were described by W. E. Davies,[21] W. H. Freeman[22] and J. Roberts,[23] who devised processes based on the incorporation of coke and non-caking coal prior to carbonisation (*v. supra*, South Metropolitan process).

One very important and much-discussed problem is to ascertain whether it is commercially feasible to subject boiler fuel to carbonisation at low temperatures prior to combustion. It is well known that experiments have been made at a Newcastle

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[17] *Proc. South Wales Inst. Eng.*, 1922, **38**, No. 2; *J.*, 1922, 580A.

[18] *Engineering*, March 24, 1922; *Gas J.*, 1921, **156**, 368, 444; 1922, **157**, 257; 1922, **158**, 449.

[19] *Cf.* Lowe, *Gas J.*, 1922, **158**, 449.

[20] E.P. 175,888; *J.*, 1922, 283A.

[21] *Gas J.*, 1922, **158**, 447.

[22] *Ibid.*, 1922, **158**, 625.

[23] *Ibid.*, 1922, **159**, 27.

Electric Power Station and the successful outcome will be of great interest and importance. The process used is carbonisation by super-heated steam using internal heating.[24]

COKE-OVEN PRACTICE.

The coking industry has been at a very low ebb owing to the industrial depression, with many plants idle or at a very reduced output. These conditions naturally have not conduced to progress. The industry is, however, intimately concerned with the development of the improved methods of cleaning coal, and the new processes of carbonisation discussed earlier.

Prominence has been given to the difference between British and American practice by several published reports on visits made to plants in the United States.[25] In American plants the ovens are customarily larger and narrower than in this country, with walls of silica brick. Flue temperatures are higher, the coal is used dry, and coking periods are shorter. The coke is smaller in size but, apparently, satisfactory to the blast-furnace managers.

The old question of the path of travel of the gases through the charge during carbonisation has again been given prominence by the work of G. E. Foxwell.[26] Foxwell's views are based on measurements of the permeability to gases of coal and coke and the plastic layer during carbonisation. He believes that the path of the gas varies during the coking period. At first, practically the whole penetrates the plastic layer and ascends through the cool central core. Afterwards, as the coked layer in contact with the oven wall thickens, and grows more porous, a bigger proportion of the gas rises through this hot zone and less through the centre until when the plastic zones are almost coalescing, the whole rises through the hot coke. Support is given to this view by an ingenious experiment of T. B. Smith,[27] who showed that ferric chloride vaporised at the oven wall passed inwards and then upwards through the charge as indicated by the stains left on the coke produced.

COAL CLEANING AND RECOVERY OF WASTE FUEL.

It will scarcely have escaped notice that a prominent feature of several proposed processes for preparing smokeless fuels is a preliminary fine grinding. This may not be such a serious disadvantage as might appear at first sight. One objection to all carbonised fuel is its inevitably increased ash content as against the raw coal. Washing, as normally practised, can usually reduce the ash-content of a coal, but still makes no impression on those mineral constituents which are more intimately incorporated in the coal substance. Thus a coke with not more than 10% of ash will, to-day, be usually regarded as satisfactory.

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[24] Merz and McLellan, W. T. Bottomley and E. G. Weeks, E.P. 171,909 ; *J.*, 1922, 48A. *Cf. Fifth Rept.*, 25.

[25] G. A. Hebden and J. W. Lee, *Gas World, Coking Sect.*, 1922, 24 ; A. H. Middleton and T. Nicholson, *ibid.*, 1922, 17, 23 ; J. Becker, *ibid.*, 1922, 135.

[26] *J.*, 1921, 193T ; *Gas World*, 1922, *Coking Sect.*, p. 64.

[27] *Gas World, Coking Sect.*, 1922, p. 52.

Recent developments in methods of cleaning coal show that it is possible to effect a much closer removal of mineral matter provided that the coal is initially broken down to a sufficient degree of fineness. The comminution of coal preliminary to carbonisation has then the advantage of making it possible to prepare a fuel with an ash-content less than would have been contemplated until recently. Thus it is claimed that the Powell Duffryn Coal Company and Minerals Separation, Ltd., will be able to put on sale in large quantities a briquetted fuel with no more than 3% of ash.[28]

The potentialities of froth-flotation continue to engross attention. E. Bury[29] has enumerated the advantages from the blast-furnace manager's point of view which may be reaped. The removal of fusain from coal is one of the most certain effects of flotation treatment, and this suffices, it is claimed, to convert some non-coking to coking coals.[30] Flotation is proposed for the recovery of fuel from washery slurry[31] and from pitheaps for the boilers of the colliery. Flotation methods also open out the prospect of making use of fine coal which is often left in the mine, where it not merely represents a loss of fuel, but also causes positive danger to the operation of the pit. Experience with flotation in America has been reported with varying results.[32] Ralston found flotation ineffective in removing ash from coke.

Some mention should here be made of the Trent process, in which the coal is first ground in water to a very fine powder, when an oil is added which is said to form an "amalgam" with the coal, leaving the mineral matter in the water phase. The coal-oil amalgam is then subjected to carbonisation to recover the oils both added and produced. New claims for this process have been recorded.[33] The cost of oils may be a factor in the success of flotation processes, especially if the finished product has to compete with industrial fuels of low value. If the product is to be carbonised with a possible recovery of oils, the prospects would seem better.

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[28] *J.*, 1922, 18R, 357R.

[29] *Trans. Inst. Min. Eng.*, 1920-1, **60**, 243 ; *J.*, 1921, 835A.

[30] *Cf.* Thau, *Stahl u. Eisen*, 1922, **42**, 1153, 1242 ; *J.*, 1922, 797A.

[31] *J.*, 1922, 207A.

[32] O. C. Ralston and others, *Chem. and Met. Eng.*, 1922, **26**, 500, 1081 ; *J.*, 1922, 532A.

[33] *J.*, 1922, 241A, 243A.

The high cost of fuel encourages the development of methods of recovering the fuel values of waste products.

The Sheffield Corporation is recovering cinders from the town refuse by screening, the coarse cinder being reserved for boiler fuel, and the fine briquetted with pitch to form a domestic fuel, the output of which is expected to reach 120 tons daily.[34]

Several proposals have been made for the recovery of fuel from furnace ashes and clinker by means of froth-flotation methods. Thus, W. D. Green[35] states that ashes ground to pass a 10-mesh sieve yielded 88% of their combustible contents in this way.

Sewage sludge is a waste product, the disposal of which is an embarrassment to most large municipalities, and several attempts have been made to recover its fuel value, usually by carbonisation, with or without admixture with coal.[36] Labour costs are an important factor in such processes and the gas obtained, though high in calorific value, is apt to be rich in carbon dioxide and hydrogen sulphide. Birmingham Corporation propose to gasify the sludge and generate power in gas engines.

Here mention may be made of the development of water power. The Water Power Resources Committee has issued a final report[37] in which the potential output of British water power is put at 210,000 kw.—undeveloped though economically available and mainly in the Scottish Highlands. This is equivalent to 40% of the output of public generating stations and an annual consumption of 3,000,000 tons of coal.

POWDERED FUEL.

A revised edition of L. C. Harvey's report on powdered fuel has been published with accounts of more recent developments.[38] Other publications traversing the same ground have been made by P. Trion and others,[39] J. Blizard[40] and R. F. Bacon and W. A. Hamor.[41]

A proposal has been made to use the powdered fuel for making gas. The powdered coal is fed intermittently into the top of a gas producer, kept hot enough to drive off volatile matter, leaving a residue to fall upon a bed of coke which is gasified by periodical blasts of steam. The gas is thus a mixture of coal and water gas.

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[34] *Fuel*, 1922, p. 259

[35] *Chem. and Met. Eng.*, 1922, **26**, 701 ; *J.*, 1922, 359A.

[36] *Cf.* F. S. Sinnatt and W. T. Lockett, E.P. 176,053 ; *J.*, 1922, 282A.

[37] *J.*, 1922, 63R. See *Fifth Rept.*, p. 27.

[38] H.M. Stationery Office.

[39] *Chaleur et Industrie*, 1921, **2**, 500 ; 1922, **3**.

[40] *Bull.* 54, *Mines Branch, Dept. of Mines, Canada.*

[41] " *American Fuels.*"

This recalls the Marconnet powdered fuel producer.[42] In installations burning powdered fuel disposal of ash is frequently effected by way of the stack. Although thereby smoke production may be avoided it would be replaced by a " grit nuisance " if the practice became extensive and this would run foul of the proposed new legislation against atmospheric pollution. Washing out or settling the grit is possible, but would involve additional outlay and operation for the auxiliary plant. Powdered fuel high in ash can, it is claimed, be burned with as high an efficiency as good clean coal—a great advantage. Moreover, the " smalls " and " breeze " from such processes as those of low-temperature carbonisation might be ground to powder, realising thereby some of the advantages of gasification.

PEAT.

A committee of a Commission of Enquiry into the Resources and Industries of Ireland has issued a comprehensive report on the potentialities of Irish peat resources.[43] The results of tests of the carbonisation of peat at low temperatures were not encouraging. Carbonised at high temperatures, peat yielded an illuminating gas when purified, but as the crude gas contained 30% of carbon dioxide the purification costs would be prohibitive. The use of peat for generating electrical power, whether by steam-driven or gas-power stations (with ammonia recovery) is regarded as the most promising outlet and it is recommended that a station of 20,000 kw. capacity should be installed.

G. Keppeler[44] gives a comprehensive survey of the problem of ridding peat of water, but concludes pessimistically that there is no immediate prospect of a solution. The most promising field is the development of mechanical appliances to facilitate the winning and handling of peat to be air-dried as at present.

J. W. Hinchley,[45] however, is more optimistic, believing that a hot-pressing process may be made effective.[46]

LIGNITE AND BROWN COALS.

Lignites and brown coals, though inferior fuels, usually occur in very thick deposits near the surface. They are thus easily and cheaply won, and this counts for much, especially when good coal has to be transported from a distant source. In Germany, even near good coal fields, the extraction and use of lignites has made great strides and the technology of the subject has been highly developed.

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[42] *Gas World, Coking Sect.*, April, 1917.
[43] *J.*, 1922, 355R.
[44] *Brennstoff-Chem.*, 1922, 3, 237, 249, 262 ; *J.*, 1922, 847A.
[45] *J.*, 1922, 365T.
[46] *Cf.* also W. Ostwald and A. Wolf ; *J.*, 1922, 972A.

W. A. Bone[47] has given a useful account of the lignites and brown coal deposits in different parts of the world and especially of the Morwell brown coals of Victoria in Australia. He has pointed out that if the raw brown coal is heated to 250°–375° C., as by hot flue-gases with low oxygen content, water and carbon dioxide are evolved, with the result that a more effective and higher grade fuel is obtained without appreciable loss of total heating value. Thus, an addition has been made to a Babcock boiler plant so that the brown coal, while being fed by gravity down a chute with louvred sides to the grate, is exposed to direct contact with hot products of combustion. In this way the fuel is dried and "up graded" before arriving at the grate and its superiority is shown by a much increased rate of steaming. The utilisation of lignite deposits in this way for the generation of power on a very large scale is said to be in process of development by the Provincial Government—another example of the tendency to get over a local shortage of good coal by the exploitation of low-grade fuels. Proposals to exploit the lignites in South Australia have also been made.[48]

M. Laffargue and R. Jaugey[49] have made a laboratory investigation of the distillation of lignites and the optimum temperatures for the production of the various products. The best results in these experiments were obtained with a temperature of 750° C.

The study of the oxidation of lignites under pressure has bulked largely in the work of F. Fischer and collaborators of the Coal Research Institute, Mülheim. Their results are held to point to the existence of an aromatic structure in the coal substance.

LIQUID FUEL.

So far as liquid fuels are concerned, a striking feature is the very widespread concern for the supplies of motor spirit in the future. By reference to the pages of the *Journal* it will be seen that commissions and committees in many countries are examining and reporting on this problem so far as it concerns their own conditions. The potentialities of alcohol have been much discussed and are receiving investigation. In this connexion the publication of a monograph on "Power Alcohol," by G. W. Monier-Williams, may be mentioned.

A British Report has been issued by the Department of Scientific and Industrial Research, 1921,[50] giving a survey of the prospects of alcohol as a petrol substitute. It shows that the possibilities of manufacture from vegetable starch in this country are remote. The use of the soil for food crops must have priority. In 1922 we are supposed to have had a surplus crop of potatoes, which raises the question whether such a result can be permanently achieved. Some experiments have been made on the cultivation of Jerusalem artichokes as a source of sugar, but the scope is limited. In the colonies and dominions overseas there are a number of potential sources of alcohol, *e.g.*, molasses, waste sulphite liquors.

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[47] *J. Roy. Soc. Arts*, 1922, **70**, 342.
[48] *J.*, 1922, 175 R.
[49] *Ann. des Mines*, 1922, **12**, 1, 327.
[50] *J.*, 1922, 13 R.

The Empire Motor Fuels Committee[51] gives an account of Ricardo's tests of undenatured alcohol as fuel in internal-combustion engines under varied conditions. Alcohol proved to be thermally more efficient than petrol or benzol at both high and low compressions and varying speeds. No corrosive action on the engine was observed under any conditions.

The carbonisation of coal is, of course, an established method of preparing motor fuel. There is an impression abroad that the oils obtained by carbonising coal at low temperatures must contain a large proportion of usable volatile spirit, but this is not necessarily true. The primary distillation products are often rich in oxygenated constituents of low volatility. They also tend to contain a large proportion of unsaturated and "gumming" compounds, the removal of which involves large consumption of acid and loss of yield. In these respects the more drastic high-temperature distillation has the advantage.

F. Fischer[52] has reported the results of experiments on increasing the yield of motor spirit from low-temperature tar by the use of hydrogen at 700°-800° C. This action was known to reduce toluene largely to benzene and cresol to toluene and benzene.[53] As would be expected, it operates in converting the phenols which form such a large fraction of low-temperature tars, into aromatic hydrocarbons. This reaction is believed to be one responsible for the formation of benzene and its homologues in normal coal distillation. By suitable treatment, preferably under pressure, he was able to get a total yield of motor spirits equal to 5·25% of the coal distilled (13 gals. per ton).

The problem has been also attacked by studying the hydrogenation of individual phenols and fractions containing tar acids, both in the laboratory and on a larger scale. The reduction is favourably influenced by the use of tin-lined iron reaction tubes.[54]

At this point reference may be made to the action of the National

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[51] *Interim Rept.*; *J.*, 1922, 123R.

[52] *Brennstoff-Chem.*, 1921, **2**, 327, 347; *J.*, 1922, 46A.

[53] *Cf.* Dufton and Cobb, *J.*, 1920, 511A.

[54] *J.*, 1922, 891A, 931A.

Benzole Association in establishing a joint Committee with the University of Leeds to direct research towards improving the technology of benzole production. Work has already been started.

ORIGIN AND CONSTITUTION OF COAL.

Though only remotely connected with industrial fuel problems, the photo-synthesis of formaldehyde and carbohydrates from carbon dioxide and water by E. C. C. Baly, I. M. Heilbron and W. F. Barker[55] is worthy of note as supporting what has been regarded as a possible mode of formation of vegetable matter from which our coal supplies are derived. More recently E. C. C. Baly, I. M. Heilbron and D. P. Hudson[56] have adduced evidence to show that the formaldehyde so produced reacts with potassium nitrite to form products which rapidly condense to give nitrogen compounds. In this way the production of the protein vegetable matter finds a plausible explanation.

F. Fischer and H. Schrader[57] have adduced further arguments in support of their theory that in the formation of coal the cellulose of vegetable matter is completely dissipated by bacterial action, and that the lignin portions survive and become finally transformed to the ulmin matter of coal. The view that coal is cellulosic in origin is controverted. This lignin theory has not received general acceptance. D. T. Jones and R. V. Wheeler[58] regard their conclusions as not proven, and see no reason to assume the survival of one type of the original molecular structure to the exclusion of others. E. Donath and A. Lissner[59] accept the theory as a partial explanation but regard it as incomplete in ignoring the vegetable and animal proteins.

The measurement of the heat change of carbonisation of fuels, which has in the past attracted interest in many quarters, has again been attempted. K. Sieben[60] has stated values for different fuels, for wood 14%, peat 12%, lignites 3–7%, and coal 0–3% of the heat of combustion of the original substance.

H. Strache and H. Grau[61] and E. Frohn[62] point out that heat of the carbonisation operation is the net value as the liquid products are in the vapour state during carbonisation. They attempt to correlate the figure with oxygen content and claim to have shown that when this is above 17% the net heat is positive and when below is negative, and the reaction is endothermic. It is important, if possible, to ascertain the value of the heat of carbonisation, which is for coals only a very small fraction of the total calorific value of the fuel. It has a bearing on the feasibility of such attractive schemes as carbonisation and gasification of coal with internal heating with oxygen,[63] and with electrical heating which has also had its advocates.[64]

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[55] *Chem. Soc. Trans.*, 1921, **119**, 1025; *J.*, 1921, 633A.
[56] *Chem. Soc. Trans.*, 1922, **121**, 1078; *J.*, 1922, 609A.
[57] *Brennstoff-Chem.*, 1922, **3**, 65; *J.*, 1922, 207 A; *Fuel*, 1922, **1**, 113.
[58] *Fuel*, 1922, **1**, 91.
[59] *Brennstoff-Chem.*, 1922, **3**, 231; *J.*, 1922, 847A.
[60] *Ibid.*, 1922, **3**, 209; *J.*, 1922, 658A.
[61] *Ibid.*, 1921, **2**, 97; *J.*, 1921, 289A
[62] *Ibid.*, 1922, **3**, 327; *J.*, 1923, 4A.

S. R. Illingworth[65] has elaborated views on the constituents of coal and the mechanism of the coking process. Coal is regarded as a conglomerate of four types of compounds, ulmins, soluble in aqueous potash solution, so-called α-compounds insoluble in pyridine, β-compounds soluble in pyridine but insoluble in chloroform, and γ-compounds soluble in pyridine and chloroform. The character of a coal is considered to be determined by the properties, including the relative thermal stabilities, of these components. He attempts to correlate these characteristics with Seyler's classification according to ultimate composition. A study of the thermal decomposition of several bituminous coals showed that they differed in the relative thermal stabilities of their components decomposing below 500° C.—the β and γ constituents. The β-components were first decomposed, the γ-constituents next, and the α-compounds above 450° C. As a generalisation, at least 5·5% of the γ-compounds, which are considered to supply the cement, must be present to permit the formation of a coke. The hardness of the coke is determined by the quantity of cement and its porosity by the volume of gas being evolved as the cement is just setting and thus fixing the cellular structure. The β-compounds being already destroyed and the α-compounds still stable, they have no influence on the structure of the coke.

R. V. Wheeler and R. Wigginton[66] have discussed the existence of resins in coal. Although their presence is to be expected, in view of the origin of coal, yet, owing to the transformation of the resins having so far progressed in the process of coal formation as to render them insoluble in alcohol and ether, it is difficult to obtain chemical evidence for identification, since the quantities extractable are so minute. There are, however, a few examples on record of the discovery of actual resin enclosures in the coals.

W. S. Gresley[67] states that he has observed resin enclosures several times in British and American coals, and G. W. Himus[68] reports observations of resinous inclusions in Manchurian coal. W. A. Bone, A. R. Pearson, E. Sinkinson, and W. E.

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[63] *Cf. Ann. Repts.*, 1920, **5**, 34.

[64] A. Helfenstein, *Z. angew. Chem.*, 1922, **35**, 73.

[65] *Fuel*, 1922, **3**, 17, 30, 49, 65, 89; *J.*, 1922, 111 T, 133 T.

[66] *Ibid.*, 1922, 10.

[67] *Ibid.*, 1922, 29.

[68] *J.*, 1922, 332 T.

Stockings,[69] in experiments on the action of solvents on coal, believe that they have obtained a "resene" by a certain method of extraction, that the coking propensity of coal is not due to resinic compounds, and that the action of pyridine is to depolymerise the coal. They dispute Illingworth's theories as to the process of coking, but their own views as expressed in this paper have been criticised.

G. S. Haslam and R. V. Wheeler[70] discuss the application of contact photographs of coal sections to the elucidation of coal structure. The method seems to offer a speedy means of estimating the relative proportions of the banded constituents (see below), since these affect a photographic plate differently.

NITROGEN AND SULPHUR OF COAL.

The minor constituents of coal have attracted a considerable amount of interest of late. Nitrogen and sulphur, though forming normally only 1–2% of the coal by weight, represent in the aggregate enormous stores of these elements in the combined state. Both have to be imported in large quantities, and yet the stores in coal are drawn upon only to a slight extent. Broadly speaking, only the nitrogen of coal which is carbonised, and of that not more than one-fifth, is recovered as ammonia. With minor exceptions the nitrogen of the coal which is not carbonised is lost. This nitrogen, if lost, is at any rate in the innocuous form as free nitrogen. Of the sulphur of coal, again only the volatile sulphur produced in town's gas carbonisation is normally recovered—in the coking industry it is mostly lost—while the rest in coal otherwise consumed is entirely lost, but here in such a condition as to be positively injurious to all forms of life and many materials. The fact is that there is no practical means of removing the bulk of the sulphur from coal until it is first gasified.

Progress in the recovery of nitrogen and sulphur requires a deeper insight into the chemical structure of elements in the coal substance. There has been a diversity of opinion as to the availability of the nitrogen left in coke after carbonisation, especially when heated in hydrogen (the so-called Tervet reaction). A. C. Monkhouse and J. W. Cobb[71] showed that it depends on the mode of preparation of coke taken, and on the atmosphere in which the coke is heated. Whatever may be the chemical nature of the nitrogen in the original coal, it is found after carbonisation in three conditions. Simple heating alone at a low temperature eliminates a portion of the nitrogen of coal as ammonia, and this proportion increases

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[69] *Proc. Roy. Soc.*, 1922, **A100**, 582; *J.*, 1922, 240 A.

[70] *Fuel*, 1922, **1**, 43.

[71] *Trans. Inst. Gas Eng.*, 1922, 137; *A.*, 1922, 532 A.

as the temperature is raised until a limit is attained which is usually less than 20% of the original nitrogen of the coal. Although another portion is liberated as free nitrogen, the bulk of the residue remains in the coke and untouched by heat alone, however prolonged. If, however, such a coke be heated in an atmosphere of hydrogen a further proportion of the nitrogen may be set free as ammonia, the proportion depending on the mode of preparation of the coke. It may be considerable in a low-temperature coke and negligible in a hard metallurgical coke, which has suffered prolonged heating at a higher temperature. By the most prolonged heating of a low-temperature coke in hydrogen Monkhouse and Cobb obtained only about two-thirds of the nitrogen as ammonia. The rest, though practically inert to the attack of hydrogen, could be readily and almost quantitatively set free by heating the coke in steam, and this is true of the nitrogen in high-temperature coke, although here the rate of liberation is slower. Thus the nitrogen of coke seems to be present in three forms, all of which may be present if the carbonisation has been made at low temperature, while one only—the nitrogen set free by steam—is present in high-temperature coke. Cokes prepared at intermediate temperature contain nitrogen with intermediate properties. The liberation of nitrogen from a hard coke by steaming differs from the other two processes in that the simultaneous gasification of carbon is an essential concomitant, whereas the elimination of nitrogen by heat and the attack of hydrogen leave the carbon intact. That the gasification of nitrogen and carbon in steam proceed *pari passu*, was put forward by H. Salmang,[72] although with inconclusive experimental support. The results of a study of this problem now in progress point to the essential correctness of Salmang's statements.

The fate of the ammonia once set free from coal in carbonisation or gasification processes depends on the treatment it has received before reaching the cooler parts of the plant. It is almost completely unstable at the temperatures current in normal practice, and given time, would break down into its elements. Some of the nitrogen of the coal is set free uncombined, and forms part of the nitrogen found in the coal gas. This proportion is roughly equal to that recovered as ammonia, indicating that considerable decomposition has probably occurred—whether by simple dissociation or by direct oxidation by indrawn air. In some quarters the suggestion has recently been made that oxidation is responsible for the more serious share of the loss of ammonia, but this has been controverted by H. D. Greenwood and R. A. Mott, in collaboration with H. J. Hodsman.[73] They found that oxygen, if present in coal gas, was preferentially removed by the hydrogen always present before ammonia could be attacked. The undoubted deleterious action of indrawn air in practice would seem to be due rather to local overheating, for the rate of dissociation of ammonia at working temperatures is very sensitive to temperature. The rate of dissociation was also found to be *materially influenced by the atmosphere, whether of nitrogen, coal gas, or hydrogen, and especially* by the presence of water vapour. Water vapour retarded both the dissociation and oxidation of ammonia. The important influence of the nature of contact materials, especially coals and the ash of coke containing iron in certain forms, was shown in these, and in the experiments reported by G. E. Foxwell,[74] in a paper bearing on the problem.

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[72] *Dissertation, Aachen*, 1914; *J.*, 1919, 452 A.

[73] *J.*, 1922, 273 T; 1923, 4 T.

The work of Monkhouse and Cobb (*loc. cit.*) bore also on the liberation of sulphur from coke. A soft low-temperature coke, containing about one-half of the sulphur present in the original coal, gave up little of its sulphur when simply heated in an inert atmosphere. The sulphur which could not be dislodged by heat alone was set free as hydrogen sulphide by the action of heat in an atmosphere of hydrogen, and almost completely if temperature and time were adequate. This was true even of hard coke prepared in the laboratory at 1100°, but the validity of this statement when applied to metallurgical coke has been questioned by A. R. Powell (private communication). This agrees with the conclusions of J. P. Wibaut,[75] confirmed by experiments on synthetic products made by heating together carbon and sulphur.

Thus the sulphur compounds differ in some respects from the nitrogen compounds. The sulphur could also be liberated by steam. Doubtless the desulphurisation of coke by hydrogen and steam goes some way in the carbonisation process, but the experiments recorded show that the process cannot go very far in practice, owing to the short time available, and do not hold out good prospects for the commercial desulphurisation of coke, however prepared.

The liberation of sulphur from a Silesian coal when carbonised at different temperatures has been studied by F. Foerster and W. Geisler.[76] They conclude that the sulphur of the iron pyrites is the source of the hydrogen sulphide evolved on carbonisation.

COAL ASH.

R. Lessing[77] emphasizes the importance of the study of the mineral matter—the dirt—of coal, both from the point of view of

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J., 1922, 114 T.

[75] *Rec. Trav. Chim.*, 1922, **41**, 153; *Brennstoff-Chem.*, 1922, **3**, 288; *J.*, 1922, 13 A, 281 A, 888 A.

[76] *Z. angew. Chem.*, 1922, **35**, 193; *J.*, 1922, 401 A. *Cf.* Powell and Parr, *Ann. Repts.*, **5**, 40; **6**, 50.

[77] *Fuel*, 1922, 7.

elucidating the origin and structure of coal, and of advancing the technique of preparing coal for the market. He maintains that[78] a treatment of the coal with dilute acid loosens the union of the constituents and the ash, thereby facilitating the mechanical separation by washing and concentration.

The importance of the ash constituents in affecting the decomposition of ammonia liberated during carbonisation while the gases are passing through the charge is indicated by Foxwell's experience[79] on the dissociation of ammonia in contact with coke containing ash of different composition and the work of H. J. Hodsman, H. D. Greenwood and R. A. Mott (*loc. cit.*).

A. Grounds[80] has examined the ashes of South Wales anthracites and particularly the ashes of the components of the coal.

THE STRUCTURE OF COAL.

F. S. Sinnatt and N. Simpkin[81] have continued their work on the ankerites of Lancashire coals by a study of the forms of iron present. The nature of the iron is very variable, but pyrites predominate. Little is soluble in water, but a considerable proportion may be soluble in hydrochloric acid and some may occur as silicate.

The palæobotanical study of coal seems to have an increasing importance. Coal has an obviously banded structure, the layers differing even to the naked eye. Four distinct structures have been recognised in these bands, and the names fusain, durain, clarain, vitrain have been given them by M. C. Stopes, who has studied their characteristics.[82] Fusain has long been known under various names (mother of coal, mineral charcoal). It is the soft, friable constituent which blackens the hand when touched. It is supposed to represent the residuum of the most resistant plant constituents after oxidation, bacterial action, and removal of "ulmic" substances. Durain is hard, dull and opaque in appearance; it contains the residues of completely disintegrated plants and is full of spores when examined in sections. Clarain is clear in contrast to the opaque durain, but, although translucent in thin sections, contains traces of plant structure. Vitrain is the bright constituent with a conchoidal fracture like pitch, structureless, like a hardened jelly. M. C. Stopes insists on reserving the name vitrain to material which shows no structure.[83]

F. V. Tideswell and R. V. Wheeler[84] have advanced the view that vitrain is derived from the dopplerite occasionally found in peat beds. Dopplerite is a black jelly-like substance—ulmic in chemical character—and an Irish specimen examined showed some resemblance (both physical and chemical) to the vitrain of bituminous coal.

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[78] *Colliery Guardian*, 1922, 1211; E.P. 173,072; J., 1922, 130A.

[79] *J.*, 1922, 114T.

[80] *J.*, 1922, 88T.

[81] *J.*, 1922, 164T; *cf. Ann. Repts.*, 1921, **6**, 12.

[82] *Ann. Repts.*, 1920, **5**, 38.

[83] *Fuel*, 1922, 22, 93.

[84] *Chem. Soc. Trans.*, 1922, **122**, 2345.

Not only do these constituents differ much in appearance and origin, but also in properties which affect their fuel value. Thus fusain, which is soft and not coherent, is relatively rich in ash, readily ignited and absolutely non-coking. These properties cause it to accumulate in the finer portions of coal and washery slurry and render its presence in a coking slack undesirable. Nevertheless, the same properties may make it quite suitable for dust firing. It is easily separable by flotation.

F. S. Sinnatt[85] has made a study of the properties of, and effects traceable to, fusain in Lancashire coals. It is present to the extent of 1–2%. Lower in volatile matter and higher in ash than the other constituents, it is undesirable if the coal is intended for carbonisation. It reduces the average percentage of volatile matter and diminishes the caking power of the coal. Coal was shown to fracture preferably along fusain bands, and in view of its softness it is not surprising that fusain was found to concentrate in coal dust, whether underground or about the screens above, or in the washery slurry. There is at some coking plants a practice of re-incorporating washery slurry with the slack to be charged, a practice which can only lead to the deterioration of the quality of the coke.

While fusain is easily separated on the large scale, the other constituents present greater difficulties. This is unfortunate, for the constituents differ markedly in important properties while fusain is only a minor ingredient amounting to a few per cent. of the total coal. Vitrain and clarain seem to have the best coking properties, though few coals have been studied and generalisation is premature.

The difficulty in separating and estimating the proportions of the banded constituents of coals is responsible for the limited amount of information which has been accumulated and the small number of coals examined from this point of view, although its importance is obvious. F. S. Sinnatt[86] has estimated the proportion of the constituents in some Lancashire seams by direct measurement *in situ* and suggested a method of charting the results. The agglutinating values of the four constituents were measured and the highest values were obtained for the clarain; in one case the value was greater for durain than for vitrain.

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[85] *Trans. Inst. Min. Eng.*, 1921, **63**, 307; *J.*, 1922, 698A.
[86] *Ibid.*, 1922, **62**, 307; *J.*, 1922, 698A.

A. Baranov and W. Francis[87] have made a similar examination of a seam of the East Kirkby Nottingham coal. It was mainly composed of durain (75%) with 12% of clarain, 5% of vitrain and, as usual, about 3% of fusain. The durain of this coal did not coke at all, while the clarain gave a strong, dense coke which could be matched by coking a mixture of four parts of the durain with one part of the vitrain.

A. Grounds[88] has made an investigation into the components of a number of South Wales anthracites. The principal constituent was a glossy substance resembling vitrain in appearance, but so dense that it was not possible to prepare a translucent section. Grounds, quite needlessly, calls it ψ-vitrain. Fusain was present to the extent of about 1% and also a component resembling the clarain of bituminous coals. The fusain presented abnormalities and was noteworthy as containing more volatile matter than the coal (anthracite).

The method of separation hitherto employed in laboratory researches on these substances has been simple hand picking. The common methods of separation in practice fail, as the differences of specific gravity in question are too small. W. R. Chapman[89] has, in preliminary experiments, found some indication of the possibility of concentrating, if not separating, the dull and bright portions. A. E. Findley and R. Wigginton[90] found some indication of differences between the constituents under the influence of an electric field.

The growing importance of the structure of coal gives an increased interest to methods of preparing sections for examination. J. Lomax, a pioneer in this art, has given a concise account of his technique which should be useful.[91]

COAL ANALYSIS AND TESTING.

It is remarkable how meagre is the published well-authenticated information about the properties of the different British coals. Though some users have accumulated a store of data for private use, *e.g.*, as to gas-making qualities, the only published large-scale systematic carbonisation tests of British coals were accumulated by the German Gas Engineers' experimental station at Karlsruhe. It is one of the objects of the Fuel Research Board to study and classify the British coal seams, especially as regards suitability for industrial use. Such work, involving physical and chemical study and working tests, would prove a protracted task for many workers, and it has been decided to delegate some work to local committees. In pursuance of this policy, the Board has recognised the Lancashire and Cheshire Coal Research Association as the Committee to undertake the physical and chemical survey of the coal resources in its locality.

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[87] *Fuel*, 1922, **1**, 219; *J.*, 1923, 41A.
[88] *J.*, 1922, 88T.
[89] *Ibid.*, 1922, 53.
[90] *Ibid.*, 1922, 106.
[91] *Ibid.*, 1922, 79.

Obviously such a chemical survey presupposes uniformity of analytical practice among those concerned, for much of coal analysis is *essentially empirical. There has been, hitherto, no such agreement among British chemists in commercial and scientific* work on coal, and to remedy this defect the Fuel Research Board has appointed a Committee to draw up methods which may be expected to command as far as possible general approval and adherence.[92]

The simple determination of volatile matter is very important, and the subject of unending discussion.[93] Fritsche recommends the aluminium retort of Fischer and Schrader,[94] but surely this is only valid where the low-temperature distillation of coal is in question. The demarcation between the fixed and volatile matter of coal is very vague and largely a question of analytical convention and the object of the analysis. The method of determining the volatile matter in a crucible heated in the Bunsen flame, as specified by the American Chemical Society, has been largely adopted, but the use of a platinum crucible is a serious obstacle to its universal adoption. It has been questioned[95] that the use of platinum is essential, and the use of crucibles of Monel metal and perhaps of other cheap materials has been suggested.

R. Lant and E. Lant-Ekl[96] advocate the determination of sulphur in coal—which is important, and has its special difficulties—by combustion in oxygen.

A. Weighell[97] has reported the results of measurement of the agglutinating power of a number of Durham coals.

Several systems of classification of coal according to composition and properties have been proposed but with partial success only, for it is obviously impossible to draw precise distinction of class where the properties and composition show no sharp gradations. T. J. Drakeley[98] has proposed a graphical method based on the relative proportion of carbon, hydrogen, and oxygen, which are regarded as constituting the true coal substance. Taking the sum

[92] *J.*, 1922, 34R.

[93] *Cf.* Delmarcel and Mertens, *Bull. Fed. Ind. Chim. Belg.*, 1921, **1**, 5, 75; *J.*, 1922, 45A. St. Claire Deville, Soc. Tech. Ind. du Gaz, June, 1922; *J.*, 1922, 698A. J. A. Maclachlan, *J. S. Afr. Chem. Inst.*, 1922, **5**, 6. Also Fritsche, *Brennstoff-Chem.*, 1921, **2**, 337, 361, 377; 1922, **3**, 4, 18; *J.*, 1922, 128A.

[94] *J.*, 1920, 566A.

[95] P. Wedgwood and H. J. Hodsman, *J.*, 1922, 372T.

[96] *Brennstoff-Chem.*, 1921, **2**, 380; *J.*, 1922, 89A.

[97] *J.*, 1922, 17T.

[98] *Chem. Soc. Trans.*, 1922, **121**, 221; *J.*, 1922, 165A.

of these as 100, the composition of the coal can be indicated on a right-angled triangular diagram, carbon and hydrogen in vertical and horizontal co-ordinates and oxygen by the distance from the hypotenuse. The points for coals, lignites, peat, and wood li in a narrow band on this diagram, and are segregated into areas according to type. Drakeley believes that the dividing line o types, say coking and non-coking coals, is quite sharp, though thi does not seem to be clearly established. Cannel and fusain do no fall within the band and this is taken to indicate a different origin

GASEOUS FUELS.

The industry of public gas supply is still in the state of transition imposed by the Gas Regulation Act of 1920, which, in bringing the conditions of statutory control and finance into line with post-war conditions, altered the system of charging for gas to one based on heat units supplied. For this purpose the unit is 100,000 British thermal units, being termed a " therm." This is essentially rational and equitable, as between supplier and consumer, but the tendency of the latter to suspect the strange new unit of charge has been increased for the time being by the peculiar manner in which a certain section of the Press has interpreted its function of enlightening the public.

For some time there has been a widespread tendency to distribute gas of lower calorific value, *i.e.*, to gasify a portion of the fixed carbon of the coke and mix it with the richer straight coal gas. It must be remembered that in established practice only 20–25% of the heat of coal is recovered in the gas, the bulk being left in the coke. The gas engineer has largely met his increases in demand by gasifying the latter, and it is interesting to speculate as to how far the process will go. The Gas Regulation Act is so framed as to leave this to the choice of the individual undertaking, which can decide on the basis of what gas it can make and supply most efficiently and cheaply.

The tendency to distribute gas of lower calorific value has, for the present, been arrested as a result of the operation of changed conditions. Indeed, the past year has seen a number of undertakings increase the declared calorific values of the gas. Now the consumption of town's gas shows a steady growth, and if this is to be met by an increased output of high-grade gas, there will necessarily result increased production of coke, unless the manufacture of carburetted water-gas is still more widely practised, which depends to a great extent on the price of oil for carburetting.

Moreover, it seems clear that much solid fuel will be consumed in domestic fireplaces for a long time to come whatever developments take place in the utilisation of gaseous fuel. This is the *market which the manufacturer of rich gas requires and can cultivate by producing a coke fuel attractive in price and quality.*

It has frequently been urged that the gas industry should abandon its present-day practice and revert to carbonisation at low temperatures, but such proposals have as a rule been unable to bear financial scrutiny.

The development of such ideas as have been advanced this year (*v. supra*, p. 18) and referred to already may, however, render practicable the economical manufacture of smokeless solid fuel without offending against the canons of good gas practice.

Even to those who pursue the bolder and in many ways more attractive ideal of completely gasifying coal, the carbonisation of a certain amount at lower temperatures may have a value in producing very rich gas to be used for bringing up the calorific value of a lower grade and possibly also in providing oils for the carburetting of water-gas. The carburetting of water-gas with oil is a process which has a very high thermal efficiency. This was a significant conclusion from the study of the carburetted water-gas plant by the Research Committee of the Institution of Gas Engineers and the University of Leeds.[99] There is, then, much to be said in favour of the carburetted water-gas process provided that suitable oils for carburetting can be obtained at a satisfactory price. An enriching gas and a carburetting agent might both come to be self-provided by the gas industry itself by the use of low-temperature carbonisation plant, furnishing also a certain quantity of smokeless solid fuel.

During the past year public attention was directed in the daily press to the carbon monoxide content of coal gas, and the consequent danger of poisoning. It might be inferred that the presence of carbon monoxide in gas was some new thing, and that its possible danger had never been considered. Coal gas has always contained carbon monoxide, usually about 7%, though sometimes as much as 10–11%, and the products of incomplete combustion of hydrocarbons initially free from carbon monoxide may also contain similar proportions. The Gas Regulation Act of 1920 recognised that to secure conservation of coal and the supply of cheap gaseous fuel it was desirable to contemplate the gasification of some of the fixed carbon of coal. This would involve a corresponding increase in the average carbon monoxide content of the gas, and a Departmental Committee was set up to report on how far the consequent increase in the poisonous quality of the gas would justify a restriction of the carbon monoxide content. In their report, which was only issued after very full enquiry (Cmd. 1422), their conclusion was stated :—

" After weighing very carefully all the facts concerned, we have concluded, on the balance of advantage to the public, that we are justified in recommending non-limitation. We have not ignored the increased risk from the poisonous nature of carbon monoxide but, when all practicable precautions are adopted, we do not consider that the increased risk will be found a serious one. The danger of increased death rate is in any case of small dimensions, and against this must be set the certain improvement in the public health by the reduction of smoke and fog arising from increased use of gas."

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[99] *Seventh Rept. of the Gas Investigation Committee*: *J.*, 1922, 53[illegible]

It is, as a matter of fact, very doubtful whether the average carbon monoxide content of town gas to-day is much higher than in 1914, and whether any single fatality, accidental or otherwise, can be attributed to an increase in the carbon monoxide content of the gas supplied.

There is another aspect neglected even by many smoke-abatement advocates, who would seem to be content if visible smoke were abolished as by the exclusive use of carbonised fuel. To achieve this would be a great gain, but the dispersal of sulphuric acid in the air would still continue. There is actually no way of extracting and retaining the sulphur of solid fuel which is feasible in practice, until the fuel is first gasified; and chemical study of the problem does not hold out much hope of a solution (*vide supra*, p. 31). This is an important reason for encouraging the gasification of fuel to the utmost practicable limits. Not only would atmospheric pollution be reduced to a minimum, but there would be an economic gain as the sulphur recovered would render us less dependent on imported supplies.

H. S. Denny and N. N. S. Knibbs[100] have given an account of a test of a station (the largest of its kind in the country) generating electricity driven by Mond-gas with ammonia recovery. The station had a generating capacity of 7400 kw. and the ammonia recovered amounted to 60·4 lb. of ammonium sulphate per ton of coal. In the test, lasting one week, the gross calorific value of the cold gas was 47·8% of the total heat supplied to the plant as fuel (*i.e.*, producer and boilers) and the gas-engine efficiency was 24%. As electrical energy, of the total heat supplied 10·2% was recovered under full load, and 7·6% under half load. Tests of large power units of this kind, though not numerous in literature, are very valuable, especially when made under working conditions. The results are much inferior to those obtainable in a steam-driven power-station, and, indeed, the authors would favour the latter unless the cheapness of coal and high value of by-products made the recovery of the latter more important. In contrast to these figures are to be quoted the tests of H. A. Humphrey[101] on a similar installation where an overall efficiency of 19·7% was claimed, and also a test on a producer-gas power plant of less than one-tenth the capacity by W. H. Patcholl,[102] when an efficiency of 19·9% was claimed. The tests under discussion are criticised on the grounds that the producer plant was obsolete in pattern and in a bad state of repair. Furthermore, when erected, it was designed primarily to recover ammonia from a low-grade coal, the quality of the gas, which was to be burnt under boilers or sent to waste, being unimportant, and no attempt was made to secure thermal efficiency.

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[100] *Trans. Inst. Mech. Eng.*, 1922, I., 97.
[101] *Ibid.* 1901, I., 41.

In recent years R. V. Wheeler and his collaborators have established valuable generalisations as to the propagation of flame through mixed gases. These generalisations as to limits and speeds of propagation make it possible to calculate some properties of complex mixtures from the corresponding properties of simple gas-air mixtures. Thus, if two simple mixtures with a certain speed of propagation are mixed the resulting complex mixture will have the same speed of propagation. The oxygen for combustion will then divide itself between the combustible gases in such proportion as to allow for the production of two equal-speed mixtures. This, accordingly, should be shown by the composition of the products of combustion. W. Payman and R. V. Wheeler[103] showed that the composition of the products is in harmony with this view, and this accounts for the very different proportion in which the oxygen is taken up by hydrogen and methane when exploded together with oxygen. Bone has ascribed the mode of partition of the oxygen to the varying affinities of the gases, and has, indeed, utilised this to compare the affinities, but Wheeler considers it to be a simple corollary to the speed generalisation.

These generalisations of Wheeler have been based mainly on the properties of the commoner combustible gases. The "limits generalisation" states that if two gas-air mixtures, each at the composition at which inflammation, both either at the upper or the lower limits, is just possible, are mixed, then the resulting complex mixture will also be a "limit mixture." A. G. White[104] concludes from his own work that the limits generalisation does not necessarily hold good with organic vapours, especially if these are capable of developing a "cool flame." At the lower limits, the *limits* generalisation seemed usually to be valid, but this was by no means true with the upper limits. This has an industrial importance as it seems possible for this "cool flame" to be propagated between wide limits and under certain circumstances to give rise to a normal hot flame.

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[102] *Ann. Repts.*, 1920, **5**, 34.

[103] *Chem. Soc. Trans.*, 1922. **121**, 363; J., 1922, 359A.

[104] *Ibid.*, 1922, **122**, 2561; J., 1923, 84A.

W. Mason and R. V. Wheeler[105] have studied the conditions under which methane-air mixtures ignite in contact with heated surfaces—a subject of special importance to the mining community.

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[105] *Chem. Soc. Trans.*, 1922, **121**, 2079; *J.*, 1922, 972A.

GAS—DESTRUCTIVE DISTILLATION—TAR PRODUCTS.

By Geoffrey Weyman, D.Sc.,

Chief Chemist, The Newcastle-upon-Tyne and Gateshead Gas Company.

For the carbonising industries the year 1922 presents many hopeful signs of sure, if slow, recovery from a period of severe depression. Towards the end of the year prospects were sufficiently promising to enable coke-ovens which had been shut down for many months, to be brought into operation, while a large proportion of gas concerns were enabled substantially to reduce the price of gas in anticipation of once more extending the field of their supply. The tar products market attained a very low level during the year, but even in this case the demand considerably stiffened in the closing months; many concerns were able to tide over bad times by turning their attention to the preparation of road tar.

Owing to the uncertain margin between cost of production and ruling prices, local conditions became of extreme importance, and this factor will undoubtedly play an important part in the development of the treatment of coal.

A very hopeful sign is the increased recognition by both the gas industry and the coke-oven industry of the fact that their common object is the economical treatment of coal rather than the mere manufacture of one principal product.

Coke Formation.

The most important development of the year has undoubtedly been the recognition of the combustibility of carbonised materials as a definite property of the fuel. Two solid fuels may possess the same calorific value, but under identical conditions may burn at very different rates and attain different temperatures, and under practical conditions the same completeness of combustion may not be attained. In the past coke has been appreciated chiefly on account of its calorific value, hardness, and porosity. The latter property has been especially considered in relation to the ease with which the fuel will burn, but has not accounted for the differences found in practice between fuels produced in different ways.

The first investigators into the question of smokeless fuel assumed that the residual volatile matter remaining in low-temperature coke was largely the cause of the greater ease of combustion such products had over those produced by high-temperature processes, and in fact it seemed that the higher the temperatures employed were, the harder, denser, and the more incombustible was the coke which resulted from the coal used.

The advantages, however, of a coke as hard and dense as high-temperature coke, and yet as easily combustible as coal, are very obvious, and the manufacture of such a fuel would undoubtedly lead to very great economies in general industry as well as in respect to the domestic hearth. The work of E. R. Sutcliffe and E. C. Evans[1] is therefore of great importance. It is pointed out that combustibility is not dependent on residual volatile matter, but rather on the mechanical structure of the fuel, and that an easily combustible coke may be obtained by high-temperature treatment in the form of a dense hard coke possessing a minute pore structure. It is also recognised that the size of the fuel pieces, the bond, and the homogeneity are other factors of importance. To produce such a fuel, the coal is first washed to reduce the ash content, dried, and then ground in a ball-mill. The powder is briquetted, and the briquettes carbonised at any desired temperature in ordinary gas retorts or in internally heated retorts.[2] In the case of swelling coals it is necessary to blend the coal with a non-caking variety or with coke breeze so that the volume of the briquette does not substantially alter. It is claimed that the briquettes can be more rapidly carbonised, and with internally heated retorts large units may be used as the carbonising mass is easily penetrated by the heating gases. Combustibility is here defined as the ease with which a fuel combines with oxygen and necessarily involves the time factor. This definition will need extension when the methods of determining this property are developed. Up to the present the methods of Thörner and Bell have been used which, roughly, consist in noting the loss in weight of the fuel in successive periods of time when heated in the presence of air or carbon monoxide. In practice the coke must necessarily maintain itself above the temperature of ignition, which varies with different fuels. It would seem better to estimate the minimum air velocity necessary to effect the complete or nearly complete combination of the oxygen of the air current used when the fuel is burning without external heating.

Further light is thrown on the subject by G. Beilby,[3] who, in investigating the micro-structure of coke, finds that the cell-walls are not, as had been supposed, more or less solid, but consist rather of very fine cells or pores enclosed by vitreous carbon apparently of a specific gravity of about 1·85. Detailed observation of the formation of coke showed that the first stage of the operation results in a foam in which each bubble is a self-contained cell, but by mutual perforation at their points of contact a sponge is produced through which the gases ultimately escape. After a time rigidity sets in and gas may only escape from the cell walls. Large bubbles can only be formed in a state of complete plasticity, and hence the introduction of solid matter which cannot be absorbed breaks the foam and renders the texture dense, but leaves a minute pore structure. The belief is expressed that the conversion of the vitreous carbon into thin films by the blowing of bubbles gives rise to a very large reactive surface, which tends to high combustibility.

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[1] *J.*, 1922, 196T.

[2] *Gas J.*, 1922, **158**, 631; *J.*, 1922, 492A; *Gas. J.*, 1922, **159**, 317; E. C. Evans, E.P. 171,152; *J.*, 1922, 6A.

[3] *J.*, 1922, 341T.

Work by K. Bunte and A. Kölmel[4] on the temperature of ignition of solid fuel also has a bearing on the question. A vertical tube filled with the graded fuel was supported in an electric furnace. A thermo-couple was suspended in the coke, and air at a regulated rate passed through. A sudden increase in temperature showed when the coke reached the ignition point. Ignition temperatures so determined were for wood charcoal, semi-coke, gas-coke, and coke-oven coke, 252°, 395°, 505°, and 640° C., respectively. Increase in the velocity of the air-current or in the oxygen concentration reduced the ignition temperature. It was further found that there was no traceable relationship between the ignition temperature and porosity, but that the former depended rather on the size of the coke and the fineness of sub-division of the coke particle. When the low-temperature product was heated to 800° C. to remove traces of gas, the ignition temperatures remained unaltered.

The presence of closed cells in coke is confirmed by H. D. Greenwood and J. W. Cobb,[5] who have determined the specific gravity of the coke material and all cells, of the material and closed cells only, and of the material itself. These determinations made on coke formed at various temperatures from the same coal were examined, when it was concluded that the initial cell formation is first set up with thick walls of soft material of low specific gravity; between 550° and 850° C. the mass as a whole shrinks and the cell walls become thinner and stronger, the porosity at this stage reaching a maximum. Above this temperature the mass hardens and contracts. Apparently, owing to the presence of closed cells, or possibly of cells of extremely small size, H. J. Rose[6] finds that the specific gravity of the coke material depends largely on the state of subdivision of the powder used and, therefore, suggests grinding the powder till it passes through a 200-mesh screen before using it for the determination. In this connexion it is of interest to note the ingenious method of A. Schmolke for determining the specific gravity and porosity of coke.[7] The air in the coke and its containing-vessel is displaced with carbon dioxide. The carbon dioxide is removed from the expelled gases and the residual air measured. The displacement is said to be complete in five minutes.

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[4] *Gas- u. Wasserfach*, 1922, **65**, 592; J., 1923, 132A.

[5] *J.*, 1922, 181T. See Anderson, *J.*, 1896, 20.

[6] *J. Ind. Eng. Chem.*, 1922, **14**, 1047; *J.*, 1923, 5A.

The chief difficulty in the manufacture of dense cokes from caking coals lies in the tendency of the liquated coal to swell or froth and stick to the retort walls. Various methods of overcoming this difficulty have been advocated.

S. R. Illingworth[8] and others preheat to destroy the excess of liquating matter. The material may then be crushed before it is carbonised in stages. Illingworth's theory of coking[9] is not altogether supported by W. A. Bone and colleagues,[10] who, after further work on the extraction of coal with solvents and the determination of the coking properties of the extracted matter, come to the conclusion that the coking properties of coals are principally due to the presence in them or formation in them by heat of non-resinous substances of cellulosic origin having fusion temperatures below those at which they undergo rapid decomposition. At the same time there is no doubt that the rate of decomposition influences very materially the ultimate properties of the coke and that by carefully controlling the time factor and temperature very different results may be obtained. In this direction A. Roberts gives a long thesis in the form of a patent specification[11] in which the opinion is given that the binding material may be distilled off by slow heating and is then not available as a bond. By more rapid heating, hydrogen is liberated and carbon so concentrated in the residue that a hard firm bond is obtained. The rise in temperature must be carefully controlled so that the penetration of heat is sufficiently rapid to decompose the plastic layer before the liquated compounds have time to travel inwards and re-condense in cooler parts. There is also the possibility of the internal destruction of the binding compounds due to previous absorption of oxygen. This is of importance in feebly coking-coals, but by suitable control of the carbonising conditions the hydrogen liberated may be utilised in neutralising the effect

[7] *Stahl u. Eisen*, 1922, **42**, 1237; *J.*, 1922, 798A.

[8] E.P. 175,888; E.P. 187,328; *J.*, 1922, 283A.

[9] *Ann. Repts.*, 1921, **6**, 47.

[10] *Proc. Roy. Soc.*, 1922, **A100**, 582; *J.*, 1922, 240A.

[11] E.P. 175,319; *Gas World*, 1922, *Cok. Sect.*, May 6, p. 18. See U.S.P. 1,352,696; *J.*, 1920, 715A.

of oxidation. The ratio of "disposable hydrogen" to "disposable oxygen" after subtracting the water, should not exceed 58% for coking purposes. In order that heat may be imparted sufficiently rapidly to coke high-volatile coals narrow ovens are advocated. The mass of coking material per unit of area of heating surface should be kept as small as possible, and may amount to 29–30 lb. per sq. ft. of heating surface. With silica walls there should be provided 3·8 lb. of wall or wall-structure per lb. of coal in the retort.

In many methods of carbonisation advantage is taken of the "blending" of coal advocated by the Fuel Research Board.[12] The South Metropolitan Gas Company mix coke breeze with coal dust and carbonise the mixture by waste heat.[13] J. Roberts has proposed a similar process.[14] S. R. Illingworth[15] blends coals of different resinic content before submitting the mixture to carbonisation in stages. D. Merkle[16] blends 60% of anthracite slack with not more than 40% of coking-coal and reduces the mixture till 85% passes a 40-mesh and 95% a 20-mesh screen, before retorting.

In preparing coke from non-coking coal F. Lierg[17] finds that the amount of pitch used as a binding agent can be reduced if it is dissolved in heavy tar-oil or bitumen of high melting-point. A residue (pitch carbon) extracted by solvents from pitch and dissolved in heavy tar-oil produced a hard dense coke from non-caking coal.

LOW-TEMPERATURE CARBONISATION.

The prospects of low-temperature work cannot be said to show improvement. Although many of the technical difficulties have been overcome, and small quantities of excellent household fuel have been placed on the market, it has to be recognised that the crude oil produced has had a diminishing value, owing to the great drop in the price of fuel oil. It may be that future research into the composition and properties of low-temperature tar may discover valuable constituents, but in the meantime no great return can be expected from this product. In respect to the solid product the Fuel Research Board, in reviewing the situation,[18] states that profitable working must depend on consumers being willing to pay a price per ton somewhat in excess of that of household coal. The third product—high-quality gas—has usually been used for supplying the necessary heat required for the carbonisation, and has not usually been found too large in amount for that purpose. *The Fuel Research Board suggests its utilisation* for the purpose of enriching high-temperature gas, but here again the market value per therm must necessarily be less than the price per therm into the holders of the average town supply. Ultimately it seems likely that local conditions will be the determining factor of economic success.

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[12] *Fuel Research Board, Report on Low Temperature Carbonisation*; *J.*, 1922, 270R.

[13] See *J.*, 1922, 196T.

[14] *Ann. Repts.*, 1921, **6**, 54; *Gas J.*, 1922, **159**, 27; E.P. 187,336; *J.*, 1922, 973A.

[15] E.P. 186,085; *J.*, 1922, 889A.

[16] U.S.P. 1,407,700; *J.*, 1922, 282A.

[17] *Z. angew. Chem.*, 1922, **35**, 264; *J.*, 1922, 532A.

[18] *Loc. cit.*

An experimental plant at the Fuel Research Board's Station is described,[19] which consists of a series of coal trays superimposed on shelves in an elevator, which can be moved vertically in a gas-tight carbonising chamber so that each tray in turn is brought opposite to an opening into the chamber outside the brickwork, by which the tray may be withdrawn, the coke cakes dropped into a cooling chamber and a fresh charge introduced. Work is proceeding in the direction of making the plant entirely automatic. The products consist of about 3500 cub. ft. of about 1000 B.Th.U. gas, 13 to 17 gallons of crude oil, and 14·5 to 15·5 cwt. of coke cakes, with 4·5 to 8·5 lb. of sulphate of ammonia per ton of coal.

Many mechanical arrangements for moving or stirring the carbonising mass have been suggested, such as rotary retorts with mechanical stirring gear,[20] retorts with revolving central shafts,[21] or scraper gear.[22] The Everard-Davies system secures rapid heat transmission by a combination of external and internal heating. Twin retorts 18–36 in. thick are placed on either side of a central perforated gas duct with external heating flues on the far sides. Triangular-shaped flues are used from which a portion of the waste gases may be passed to heat the retort internally.[23]

The use of an atmosphere rich in hydrogen (60–70%), with or without superheated steam, is claimed to give higher yields of sulphate and oils. The gas rich in hydrogen is produced by cracking the medium or heavy portions of the oil in small iron tubes.[24]

Internal heating may be effected by the use of low-pressure superheated steam. In order to avoid contamination in the recovery of the sensible heat of the outgoing gases, fresh water is evaporated in heat exchangers to make up for condensation, and may be superheated before introduction into the retort.[25]

[19] *Loc. cit.* See E.P. 178,994 ; *J.*, 1922, 456A.
[20] F. D. Marshall, E.P. 186,375 ; *J.*, 1922, 930A.
[21] H. P. Hird, E.P. 184,525 ; *Gas J.*, 1922, **159**, 653.
[22] C. J. Goodwin, *Gas J.*, 1922, **158**, 624 ; *J.*, 1922, 580A.
[23] W. Everard Davies, *Gas J.*, 1922, **158**, 447.
[24] J. Moeller and L. de Fonblanque, E.P. 174,165 ; *J.*, 1922, 167A.
[25] **Merz and McLellan, W. T. Bottomley and E. G. Weeks, E.P. 171,909, 175,800, 176,149 ; *J.*, 1922, 48A, 279A.**

An interesting proposal is to force powdered coal fed through horizontal cylinders to descend a vertical retort in a shower so that it becomes heated to 400°–700° C. The retort is oblong in section, and is provided with internal corrugations.[26]

The proposal to pass powdered material through molten metal baths either at the same or different temperatures, so that the heating is accomplished in stages,[27] is fascinating, but the separation of the residue would seem to offer more difficulty than in the case when the material is liquid.[28]

The possibilities of electrical heating for gas production are discussed by A. Helfenstein,[29] but the economy of the project seems dependent on the existence of otherwise waste electrical power. The current consumption is estimated at 1·1 to 1·3 kw. per cubic metre of gas made.

Another proposed method[30] consists in suspending powdered coal in oil. It is stated that the products obtained from a mixture of coal and oil are more valuable than those resulting from the decomposition of each separately, owing to the fact that the cracking of the oil is more perfect, as by reason of its surface tension, the oil adheres to the coal at temperatures above its distillation point. The pasty mass obtained from the Trent process of separating water from oil and tar emulsions[31] would seem to lend itself to this method of treatment and can be usefully carbonised by mixing the mass with more oil and forcing the mixture through an externally-heated coiled pipe.[32]

PEAT, LIGNITE, ETC.

The development and utilisation of our peat deposits are the subject of a Report of a Commission of Inquiry,[33] in which is given a general review of the subject. While high-temperature treatment is considered to offer the greatest possibilities the large proportion of carbon dioxide (30%) is a great drawback to the yield of 10,000 cub. ft. of gas obtained per ton of peat. G. Keppeler[34] reviews methods of removing water from peat sufficiently to render it of economical quality for carbonisation and other purposes, and while the compression of the wet peat with a previously dried portion (30% of water)[35] so as to obtain a product containing about 50–60% of water offers advantages, the future development is considered to lie rather in the direction of mechanical winning, followed by stack drying. The water-holding capacity is also discussed by Wo. Ostwald[36] from the colloid point of view, and a process of steaming under pressure followed by further pressing is suggested.

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[26] J. A. Yeadon, E.P. 185,684; *J.*, 1922, 851A.

[27] T.I.C. Research Co., Ltd., A. McD. Duckham and J. S. Morgan, E.P. 176,438, 183,180; *J.*, 1922, 315A, 700A.

[28] See p. 69.

[29] *Z. angew. Chem.*, 1922, **35**, 73; *J.*, 1922, 208A.

[30] Trent Process Corporation, E.P. 159,142; *J.*, 1922, 453A.

[31] J. D. Davis, P. B. Place and G. S. Scott, *Chem. and Met. Eng.*, 1921, **25**, 182, 1131; *J.*, 1922, 92A. See also *J.*, 1921, 615A, and J. D. Davis and C. E. Coleman, *Chem. and Met. Eng.*, 1922, **26**, 173; also J. A. Chown, E.P. 173,039; *J.*, 1922, 132A.

[32] W. E. Trent, E.P. 159,497; *J.*, 1922, 243A. See *J.*, 1921, 684A; *Special Report No. 1, Fuel Research Board*, 1922, and R. L. Brown, *Chem. and Met. Eng.*, 1922, **26**, 363; *J.*, 1922, 241A.

[33] *Gas J.*, 1922, **158**, 566.

[34] *Brennstoff-Chem.*, 1922, **3**, 237, 249, 262; *J.*, 1922, 847A.

Lignites and brown coals are dealt with by W. A. Bone,[37] who refers to the interesting process of "up-grading" which consists in a preliminary heat treatment at a temperature of 250°–375° C., when a chemical condensation occurs with elimination of one-third of the total oxygen, one-tenth of the hydrogen, and only one-thirtieth of the carbon. Hence a residue is left which, when carbonised, produces a fuel of fair calorific value.

In further work of the Canadian Lignite Board[38] good results were obtained by rapid carbonisation at high temperature, a similar product being obtained to that from slow carbonisation at low temperature (590° C.). The by-products are small in quantity, and of little value.

A simple form of carbonising plant is described by E. Stansfield.[39] It is said that a mixture of 30–40 parts of pulverised black peat (35–45% of water), 8–10 parts of powdered pitch, and 80–100 parts of small coal gives on carbonisation a hard metallurgical coke of low sulphur content.[40]

CARBONISATION IN GAS RETORTS.

In recent years there has been a tendency to introduce large horizontal retort units capable of dealing with a ton of coal in a 12-hour charge. The high temperature necessary in the combustion chambers (1400° C.) to carbonise the coal efficiently, particularly in the case of Durham coal, brings an undue strain on the settings, and there is some inclination to be satisfied with charges amounting to about 15 cwt. per 12-hour charge, although this naturally depends on the coal used. The time taken for the heat to penetrate to the centre of the charge has been shown to be greatly influenced by the chemical composition of the coal. To compensate for the slower penetration higher carbonising temperatures can be used within certain limits, but although the quality of gas may be better, volume for volume, owing to the more rapid evolution of gas, the average quality is much reduced by secondary decomposition. Oxidised or slightly caking coals are found to be capable of rapid carbonisation compared with those caking coals which give heavy plastic layers during distillation. The effect of the physical condition of the coal on the results obtained by carbonisation discussed previously[41] are further investigated with the help of a coal-testing plant,[42] and an increase in the rate of carbonisation effected under the same combustion flue temperature, by regulation of the size of the coal, is found to give considerably increased thermal yields in gaseous form. H. Tindale also finds that small coal upsets the heat regulation of the settings, and yields less gas.[43] The throughput in vertical retorts decreases in the order of about 2% for every 1% increase in the weight of one cubic foot of the coal used. In the case of horizontal retorts a charge of 13 cwt. of large crushed coal, occupying 30 cub. ft., was easily carbonised in the time given, while the same volume weighing 14·5 cwt. was not only far from carbonised, but required extra heat, which, unless supplied by the use of extra fuel, resulted in a drop of temperature in the setting of 100°–150° C.

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[35] H. Caro, *Chem. Zentr.*, 1921, **92**, IV., 1347; *J.*, 1922, 45A.

[36] *Kolloid-Zeits.*, 1921, **29**, 316; 1922, **30**, 119, 187; *J.*, 1922, 318A, 319A, 972A.

[37] *J.*, 1922, 126R.

[38] R. de L. French, *J.*, 1922, 16T.

[39] E. Stansfield, E.P. 177,588; *J.*, 1922, 362A.

[40] J. W. Leadbeater, E.P. 172,199; *J.*, 1922, 46A.

The actual heat value of the decomposition of coal has not yet been conclusively established, although K. Sieben[44] argues that as the thermal losses in normal large-scale practice are equal to, or somewhat less than, the theoretical obtained by calculation there must be heat liberated in the coking of coal.

An instructive detailed paper by J. S. Thorman[45] describes a very good method of sampling coal on a large scale. To reduce loss in working producer furnaces of the step-grate type, which have a tendency to pass a large quantity of unburnt fuel, the pan-ash is returned to the fire after drawing, and before charging up with fresh fuel. A more common practice is to withdraw the ash from the base only, pushing the clinker and ashes between the upper bars back into the fire. Thorman considers that the grate area should be 1·5 sq. ft. per ton of coal carbonised per day with a depth of fuel bed of at least six feet when using large coke. The heat exchange between waste gases and secondary air is usually very poor, but may be considerably increased by a tubular system.

It is very seldom that a completely new gasworks is erected on a new site, and the results from the new installation of vertical retorts with waste-heat boilers and the purifying plant at the

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[41] *Ann. Repts.*, 1921, **6**, 49.

[42] G. Weyman, *Gas J.*, 1922, **158**, 864 ; *J.*, 1922, 532A.

[43] *Gas J.*, 1922, **157**, 31.

[44] *Brennstoff-Chem.*, 1922, **3**, 209 ; *J.*, 1922, 658A.

[45] *Gas J.*, 1922, **158**, 27 ; *J.*, 1922, 319A.

Rome Street Works at Carlisle, will be watched with great interest.[46] The steaming of vertical retorts is finding extensive application, although the advantages vary considerably with the capacity of the particular coal used for forming an impenetrable plastic layer. The movement of the coal down the retort gives the system, however, great advantages over the horizontal-retort system where steaming is more or less restricted to the period when the charge is coked, and proper contact is difficult to attain Experiments made in America do not favour the proposition in horizontal retorts unless the plant is working below full load.[47]

The use of air introduced at the base of vertical retorts to generate, internally, heat required to assist the production of water-gas by steaming, is claimed.[48]

The recent tendency has been to reduce the seals of hydraulic mains to a minimum. C. Carpenter suggests an arrangement for altering the liquor levels so that retorts may be sealed or unsealed as desired.[49]

COMBINED PLANTS—COMPLETE GASIFICATION.

From steaming in vertical retorts it is but a step to the consideration of the very large number of proposals which have been made for effecting complete or partial gasification. The independent generation of blue water-gas and subsequent mixing with coal gas has led to the close combination of the two plants, the blow gases from the former being lead into the heating flues of the latter.[50] Or, as in the "Rincker" plant, one of two twin generators may serve alternately for the carbonisation of the coal and the gasification of the coke.[51] The blow gases are used for generating steam, and after passing through one generator the gases produced pass downwards through the other generator which contains freshly-charged coal on top of the residue from previous working. A more complicated arrangement consists of twin generators with regenerative linings and a retort superimposed on a third generator.[52]

In another type of plant a vertical retort is superimposed on a single generator.[53] The run gases produced by steaming the coke in the generator are passed through the retort to help in carbonising the coal, which is also heated by the blow gases passing round the retort in external flues. A modification consists in using the heat of the blow gases to crack the hydrocarbons into permanent gases in an annular space around the top of the retort.[54]

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[46] J. E. Blundell, *Gas J.*, 1922, **160**, 94.

[47] W. A. Dunkley and R. D. Leitch, U.S. Bureau of Mines, *Gas J.*, 1922, **157**, 443.

[48] Woodall, Duckham and Jones (1920), Ltd., and A. McD. Duckham, E.P. 185,461 ; *J.*, 1922, 848A.

[49] E.P. 176,891 ; *J.*, 1922, 361A.

[50] J. Lowe, E.P. 149,928 ; *Gas J.*, 1922, **159**, 324 ; *J.*, 1922, 699A.

[51] P. Gregory, *Gas J.*, 1922, **159**, 473 ; *J.*, 1922, 738A.

[52] J. F. Simpson, E.P. 179,643 ; *J.*, 1922, 493A.

[53] Strache system, A. Breisig, *Gas- u. Wasserfach*, 1922, **65**, 509.

By gradual stages one may pass to the type of plant in which the generator is enlarged so as to include the retort. As a rule such plants do not appear to work well with strongly-caking coals, as it is difficult to maintain the carbonisation and gasification zones distinct. The Maclaurin plant[55] can produce smokeless fuel, accompanied by fair yields of oil and 25,000 to 30,000 cub. ft. of about 250 B.Th.U. gas. The Moore system appears to be a development of the Tully plant in which heat is generated by internal combustion, so as partially or entirely to gasify the fuel.[56]

A combination of methods is also proposed, in which crude gas of low quality is heated by passage through incandescent coke, and then used to carbonise coal in a retort so as to produce an enriched gas and a domestic fuel.[57]

E. Fleischer[58] suggests a shaft furnace for producing metallurgical coke by carbonisation, effected mainly by the heat of "carrier" gases. In order not to interfere with the yields of coke the heating gases entering at the base must contain little or no water vapour or carbon dioxide, but in the upper part of the furnace air and steam may be admitted without detriment, so long as the temperature does not exceed 600°–800° C.

An ingenious arrangement[59] combines steam raising in an ordinary boiler with by-product recovery. The boiler, fitted with a chain grate stoker, is started up in the usual manner. At the back of the smoke-box is a small vertical distillation retort, with helical feed. As soon as the necessary temperature has been reached the chain grate feed is reversed, and the carbonised fuel discharged from the retort is distributed over the grate. The gases from the retort are used for by-product recovery.

A modified form of Tully plant may be used to produce hydrogen for synthetic ammonia manufacture. Coal is distilled and the crude gas passed through coke at 1000°–1100° C. to decompose the hydrocarbons. The carbon monoxide is converted into carbon dioxide and additional hydrogen generated by reaction with steam in the presence of a catalyst.[60]

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[54] E. F. Murray, E.P. 185,887 ; *J.*, 1922, 849A ; *Gas J.*, 1922, **160**, 435.

[55] *Gas J.*, 1922, **158**, 325 ; E.P. 182,648 ; *J.*, 1922, 660A.

[56] S. Moore, *Gas World*, 1922, **76**, 360.

[57] G. Helps, E.P. 181,403, 181,404, 181,665 ; *J.*, 1922, 579A.

[58] G.P. 298,085 ; *J.*, 1920, 622A ; E.P. 154,938 ; *cf.* E.P. 152,650 ; *J.*, 1922, 168A.

[59] T. O. Wilton, E.P. 178,952 ; *J.*, 1922, 454A.

[60] J. H. West and A. Jaques, E.P. 181,062 ; *J.*, 1922, 579A See also *Gas J.*, 1922, **159**, 706 ; *J.*, 1922, 393B ; E.P. 188,494 ; *J.*, 1923, 45A.

A warning note is struck by H. Nielsen,[61] who explains that complete or partial gasification can hardly be more efficient than modern producer-gas practice and that some of the extreme claims put forward recently must be treated with reserve.

WATER-GAS.

In order to increase their capacity, water-gas plants are sometimes used for complete gasification, coal being substituted in part, or entirely, for coke. Certain precautions have to be taken.[62] There is certainly one advantage in using a mixture of coal and coke, and that is that the gas approximates more in composition and properties to coal gas, and is therefore easily mixed for town use.

A more novel proposal is to enrich the water-gas by introducing powdered coal suspended in a gas stream into the top of the generator, where the temperature is brought up to about 2000° F. (1090° C.). The dust particles are carbonised by the heat of the upward rising gases and the coke particles formed agglomerate and are said to sink on to the surface of the fuel bed.[63]

The reactions taking place in water-gas generation receive the attention of S. Kohn,[64] and of H. S. Taylor and H. A. Neville.[65] In the investigations by the last-named workers, steam was passed over charcoal mixed with various catalysts at a temperature of 400° to 570° C. to study the reaction $C+2H_2O=CO_2+2H_2$. Sodium and potassium carbonates were the only catalysts found to be effective; iron oxide in particular seemed to be impotent. The latter is known to exert a catalytic influence on the water-gas reaction $C+H_2O=CO+H_2$, so that it was considered that the effect of the alkali carbonates was due to an acceleration of the reaction $C+CO_2=2CO$ in this way influencing the reaction first studied. That this was possible was shown by independent experiment.

A further detailed report has been made by the Gas Investigation Committee of the Institution of Gas Engineers[66] on the working of a carburetted water-gas plant with particular reference to the use of waste-heat boilers. With an output of about 1½ million cub. ft. of 483 B.Th.U. gas, about 35½ lb. of coke and 1·8 gallons of oil were used per 1000 cub. ft. of gas made. The water evaporated from the waste-heat boilers by the "blow" gases was 70–80 lb. per 1000 cub. ft. of gas made, from and at 100° C., which, in certain tests was more than sufficient for plant requirements. Heat, water, and carbon balances are given. The efficiency was found to be

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[61] *Gas J.*, 1922, **157**, 257.

[62] W. W. Odell, *U.S. Bureau of Mines Tech. Paper* 284, 1921; *J.*, 1922, 492A.

[63] Fuller-Lehigh Co., E.P. 171,079; *J.*, 1922, 974A.

[64] *J. Ind. Eng. Chem.*, 1922, **14**, 711.

[65] *J. Amer. Chem. Soc.*, 1921, **43**, 2055; *J.*, 1922, 141A.

[66] *Seventh Report, Gas J.*, 1922, **158**, 805; *J.*, 1922, 532A.

69·7%, including recovered coke from the ashes, and would have been about 8·5% less had the steam been generated externally.

By making the "blow" and "run" periods equal, G. Vigreux[67] is enabled to use two units for continuous gas production. The waste-heat boiler assists in automatic adjustment of the conditions, as the greater the heat value of the blow gases the more steam is raised to be passed subsequently to the generator.

Vignon's results[68] as to the production of methane when water-gas is heated with steam in the presence of lime have not been confirmed.[69]

A process in which superheated steam and oil are passed over electrical heating elements coated with refractory material which functions as a catalyst[70] is said to produce 1000 cub. ft. of 495 B.Th.U. gas from 3·19 gallons of oil, which is about 1½ times the thermal yield per gallon of oil usually experienced in carburetted water-gas manufacture.

The process of Sabatier and Mailhe for cracking oil in presence of a metal catalyst is described by P. Mallet.[71] Retorts for cracking oil are covered with a coating of copper. In a trial of a plant at Brussels[72] consisting of an installation of six retorts heated by tar-burners, the liquid portion of the products is condensed and distilled for motor spirit and uncracked oil, and the uncondensed gas of high calorific value used to enrich blue water-gas or compressed for railway lighting. It seems very probable that improved methods of oil-cracking for carburetting water-gas will come into use.

The presence of iron carbonyl in water-gas has often been observed, but some striking effects of depreciation of lighting capacity of incandescent mantles, owing to deposition of ferric oxide resulting from the decomposition of iron carbonyl, are described by H. Bunte and E. Terres.[73] The formation of iron carbonyl increases rapidly with increase of pressure, but is compensated by increase in the rapidity of decomposition with a rise of temperature to over 200° C.[74] Reference may also be made to a special case of trouble due to iron carbonyl reported by H. B. Brown.[75]

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[67] *Gas J.*, 1922, **159**, 531.

[68] *Ann Repts.*, 1921, **6**, 60.

[69] H. Tropsch and A. Schellenberg, *Brennstoff-Chem.*, 1922, **3**, 33; *J.*, 1922, 166A.

[70] Van Steenbergh, *Gas J.*, 1922, **158**, 208; U.S.P. 1,407,339-40; *J.*, 1922, 321A.

[71] *Gas J.*, 1922, **159**, 475; *J.*, 1922, 739A.

[72] M. G. Goune, *Gas J.*, 1922, **160**, 34.

[73] *Gas u. Wasserfach*, 1922, **65**, 145; *J.*, 1922, 241A.

[74] R. L. Mond and A. E. Wallis, *Trans. Chem. Soc.*, 1922, **121**, 29; *J.*, 1922, 173A.

[75] *Gas J.*, 1922, **158**, 37.

COKE-OVEN PRACTICE.

Comparison of American and British coke-oven practice has given rise to considerable discussion.[76] Conservatism in this country seems to be largely due to the attitude taken up by the iron and steel manufacturers, who still appear to give beehive coke preference in the market and regard this quality of coke as more or less of a standard. The American coke is reported to be shorter and of inferior appearance, but as in the American blast-furnace practice it is becoming customary to grade the coke to a size less than 4 in. in diameter, in common with other materials, the smaller size of coke produced in that country does not appear to be disadvantageous. The coal used for coke production in America is high in volatile matter (35% or even higher) and is carbonised in a shorter period (about 18 hours). The American ovens are narrower, but greater in height and length, measuring 15–18 in. by 10–12 ft. by 38 ft. The materials used for construction are almost invariably of 95% silica content, while the temperatures of the flues run as high as 1350° C. The coke is sold on a 2½% moisture basis and almost always quenched in central stations. The yields of by-products are quite as high as those in this country, while the surplus gas often amounts to 60% of the total.

A description of the Koppers system, more used in America than in this country, is given by C. E. Wallin.[77] The ovens, constructed of silica material, have stood well for some three and a half years, carbonising coal with 11% of moisture. A feature of the installation is the attention given to automatic control and the use of recording instruments.

The dry-cooling of coke and recovery of the sensible heat by circulation of waste gases has been tried over a period of 17 days, when 23·6 tons of coke per day was cooled and a total of 9·4 tons of water at 50° C. converted into steam at 94·5 lb. pressure per sq. in. The average specific heat of coke with 10·5% of ash was found to be 0·333 between 18° and 800° C.[78]

The supply of coke-oven gas to Middlesbrough is now well established. The supply is taken from 46 ovens of the Otto regenerative type, each dealing with 9½ tons of coal per day. Duplicate mains are used for separating the richer portion of the gas, which has a calorific value as high as 570 B.Th.U. In the seven years of working there have been three partial stoppages and one complete stoppage, due chiefly to strikes.[79] At Willington, Co. Durham, a local area is supplied from a coking plant comprising 120 Semet-Solvay waste-heat ovens. The richer portion of the gas for town supply is here separated by taking a portion of the gas into a holder during favourable times. The calorific value over a period of two years is given as 476–479 B.Th.U.[80]

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[76] A. H. Thwaites, G. A. Hebden and others, *Gas World*, 1922, **76**, *Cok. Sect.*, Mar. 4, p. 10; June 3, p. 11; Aug. 5, p. 10; *cf.* J. Becker, *Chem. and Met. Eng.*, 1922, **27**, 875.

[77] *J.*, 1922, 298T.

[78] P. Schläpfer, *Stahl u. Eisen*, 1922, **42**, 1269; *J.*, 1922, 798A. See also H. Wunderlich, *Gas u. Wasserfach*, 1921, **64**, 703; *J.*, 1922, 90A.

J. F. O'Malley describes a system in which blue water-gas is used for heating the coke-ovens, thus liberating the richer coke-oven gas for town use.[81]

TAR, BENZOL, AND NAPHTHALENE RECOVERY.

Very little can yet be said of the practical possibilities of fractionally removing the tar components from gas. Investigation of the subject is being pursued mainly in connexion with the mixture of vapours arising when the condensed tar is redistilled. Mathematical treatment of problems of condensation is given by B. F. Dodge,[82] and by W. G. Whitman and J. L. Keats.[83]

A Cottrell precipitator has been used before the condenser of a wood-distillation plant[84] in order to separate pitchy matters which might contaminate pyroligneous acid, but the idea of electrical precipitation of tar fog has not, so far, attracted much attention in the carbonising industries.

The simultaneous removal of naphthalene and recovery of benzol possesses considerable advantage in the way of economy. To secure immunity from naphthalene stoppages it seems to be imperative thoroughly to scrub the gas with a suitable oil, so as to reduce the naphthalene content to less than that corresponding to saturation at the lowest temperature experienced in the gas mains. According to J. S. G. Thomas[85] this will be no more than 0·8 grain per 100 cub. ft. at 0° C. for moist gas. While it is not clearly established, it appears that coal gas prior to the oil-washing plant may carry naphthalene mechanically far in excess of that corresponding to saturation at the existing temperature, and thus oil-washing plants eliminate very much larger quantities of naphthalene than might be supposed.

The suitability of a wash oil is shown[86] by passing a regulated current of air first through crude benzol, and then through a portion of the wash oil, finally estimating any naphthalene which may be given off from the wash oil with picric acid solution.

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[79] C. F. Blincoe, *Gas World*, 1922, **76**, 378.

[80] T. Nicholson, *Gas World*, 1922, **76**, *Cok. Sect.*, May 6, p. 14; *J.*, 1922, 451A.

[81] *Chem. and Met. Eng.*, 1922, **27**, 75.

[82] *J. Ind. Eng. Chem.*, 1922, **14**, 1062; *J.*, 1923, 38A.

[83] *Ibid.*, 1922, **14**, 186; *J.*, 1922, 315A.

[84] L. F. Hawley and H. M. Pier, *Chem. and Met. Eng.*, 1922, **26**, 1031; *J.*, 1922, 495A.

[85] *J.*, 1916, 506.

[86] F. Pannertz, *Gas- u. Wasserfach*, 1922, **65**, 113; *J.*, 1922, 241A.

The South Metropolitan Gas Company do not recover benzol but wash the gas with anthracene oil, previously steam-distilled to reduce its naphthalene content to 6–8%, at the rate of 15 gallons of oil per million cub. ft. of gas.[87]

In the case of concerns which regularly produce carburetted water-gas, J. Parker[88] proposes to use the water-gas oil in the first place to wash the coal gas free from naphthalene, and afterwards use the oil for carburetting the water-gas in the usual way. The naphthalene is thus largely transferred to the water-gas tar, while the town gas contains only that naphthalene (from 6 to 8 grains per 100 cub. ft.) present in the water-gas.

In the condensation and separation of ammonia, benzene, and ethylene, C. Still[89] frees the gas from tar fog, and then compresses to 100–200 atmospheres, at the same time cooling to the original temperature in the presence of physical and chemical absorbents.

Considerable attention has been given to the use of charcoal and active carbon as absorbing agents. Experiments made by F. Fischer and colleagues[90] showed that active charcoal in cylinders absorbed considerable quantities of the richer constituents of coke-oven gas under compression which could afterwards be withdrawn in the form of gas of high calorific value (710–2237 B.Th.U. per cub. ft.) by releasing the pressure and heating. A. Engelhardt[91] describes an experimental plant for the recovery of benzol by absorption in charcoal as suggested by K. Bunte, consisting of duplicate filters containing the carbon in small granules. The carbon must be sufficiently active to absorb up to 25% of its weight of benzol from air, carrying 70 grams per 100 cub. ft. at 20° C. The gas is passed downwards through one filter till a trace of benzol shows at the outlet, when the gas is diverted to the other. The saturated filter is then steamed until the carbon reaches a temperature of 120° C., when it is left ready for further use. The benzol separated from the condensed products is of nearly 90% quality. The outlay is considered to be less than for oil-washing plants, while the maintenance is very much less. It appears evident, however, that the success of the process will depend largely on the prior removal of tar fog, which ruins the carbon. The best activated carbon is too costly for the purpose, but a quality prepared from lignite might be suitable.[92]

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[87] E. V. Evans, *Gas J.*, 1922, **157**, 373.

[88] *Gas World*, 1922, **77**, 235.

[89] E.P. 147,737; *J.*, 1922, 167A.

[90] F. Fischer, H. Schrader and C. Zerbe, *Brennstoff-Chem.*, 1922, **3**, 145; *J.*, 1922, 451A.

[91] A. Engelhardt, *Gas u. Wasserfach*, 1922, **65**, 473; *J.*, 1922, 659A.

[92] F. Fischer and colleagues, *Brennstoff-Chem.*, 1922, **3**, 241; *J.*, 1922, 851A.

E. Berl and K. Andress use the charcoal process for the determination of benzol in gas.[93] H. Bähr prefers to expel the absorbed vapours by superheated steam, while the saturated carbon is heated to 160°-170° C. by an oil jacket.[94]

The influence of water[95] and the heat evolved in the absorption of gases by charcoal[96] have been investigated. The work of W. D. Harkins and D. T. Ewing[97] is particularly interesting, and may be contrasted with the observations recently made of the influence of structure on the combustibility of coke.

AMMONIA AND AMMONIUM SULPHATE.

Investigation into the possibility of increasing the proportion of nitrogen recovered as ammonia is being pursued. G. E. Foxwell[98] in an elaborate paper discusses the thermal dissociation of ammonia with particular reference to coke ovens. The rate of the bimolecular reaction $2NH_3 + N_2 = 3H_2$ does not increase very rapidly with rise in temperature, but the structure of the material in contact with the gas (size of pore rather than porosity) influences the reaction. The chemical composition of the material in contact with the gas is also of importance, especially in respect to the presence of iron as iron oxide, which considerably accelerates the decomposition. Lime also exerts an influence in this direction, but as it assists in the liberation of ammonia from the carbonising coal in the first place, its presence may lead to an increased recovery. Sodium chloride also decreased the rate of decomposition for low values of the ratio $HCl : NH_3$, but the possibility of an increased amount of iron being ultimately liberated as metal or oxide may compensate.

A. C. Monkhouse and J. W. Cobb,[99] report the results of further experiments in the liberation of nitrogen from coke in various atmospheres. By prolonged treatment with hydrogen at temperatures up to 1000° C., 68·2% of the nitrogen in coke carbonised at 800° C. was obtained as ammonia. By gasification with steam the whole of the nitrogen was obtained as ammonia.

The possibility of loss of ammonia by oxidation during carbonisation is investigated by H. D. Greenwood and H. J. Hodsman,[100] and the general conclusion is reached that oxygen admitted into the carbonising chambers combines preferentially with gaseous hydrocarbons, and does not oxidise ammonia, but a certain loss of the latter may arise through this internal combustion causing local high temperatures.

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[93] *Z. angew. Chem.*, 1921, **34**, 278 ; *J.*, 1921, 536A.

[94] H. Bähr, *Chem.-Zeit.*, 1922, **46**, 804 ; *J.*, 1922, 803A.

[95] H. Herbst, *Biochem. Zeits.*, 1921, **118**, 103 ; *J.*, 1921, 877A.

[96] S. McLean, *Trans. Roy. Soc. Canada*, 1921, **15**, iii., 73 ; *J.*, 1922, 357A.

[97] *J. Amer. Chem. Soc.*, 1921, **43**, 1787; *J.*, 1922, 87A.

[98] *J.*, 1922, 114T.

[99] *Gas J.*, 1922, **158**, 828 ; *J.*, 1922, 532A.

[100] *J.*, 1922, 273T. See also *Gas World*, 1922, **76**, *Cok. Sect.*, Feb. 4, p. 10 ; *J.*, 1922, 166A.

More attention is rightly being given to the design of distillation plant dealing with ammoniacal liquor. P. Parrish[101] clearly shows in what direction improvement can be made and gives heat balances pointing to the excessive steam consumption often experienced. E. Piron also makes a valuable contribution.[102] The design and efficiencies of various columns are discussed by W. A. Peters[103] and W. K. Lewis.[104]

In the manufacture of ammonium sulphate L. Singer removes tarry matter from mother liquors by supersaturation with ammonia and filtration through sand.[105] Pyridine is recovered or eliminated from the salt by a process involving the use of two saturators.[106]

The production of neutralised salt reached to over 50% of the total sold in November and is likely entirely to displace the older acid qualities.[107] In most cases the neutralisation is accompanied by processes for drying and screening the salt which result in a substantially dry, friable material containing about 25·5% of ammonia. In some cases the mechanical reduction has been too severe and the dusty flour-like powder resulting has been objected to by consumers.

Considerable activity has been displayed in evolving fresh methods of neutralising and drying. T. Johnson[108] finds that it is impossible to reduce the free acid to below 0·025% with less than 2½ gallons of water per cwt. of salt, and uses a concrete mixer in which finely-divided alkali (soda ash) is mixed with the salt after discharge from the centrifuge. The neutralised salt is then dried by passage through a rotating inclined cylinder against a current of air heated by a gas burner. Twin saturators are used by J. B. Hansford in conjunction with a drying apparatus which consists of a circular tray with vertical spindle revolving in a horizontal plane and provided with ploughs to turn the salt over.[109] It is heated by gas burners underneath. In another method[110] the salt is fed downwards through a tower containing shelves and rotating arms. Ammonia gas and heated air are passed upwards. In place of the tower an enclosed spiral conveyor may be used,[111] or the salt may be led by pneumatic means to and through a conduit where it is similarly exposed to a current of hot air and ammonia vapour.[112]

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[101] *J.*, 1922, 229T.

[102] *Chem. and Met. Eng.*, 1922, **26**, 317; *J.*, 1922, 240A.

[103] *J. Ind. Eng. Chem.*, 1922, **14**, 476; *J.*, 1922, 619A.

[104] *Ibid.*, 1922, **14**, 492; *J.*, 1922, 573A. See also W. H. Rodebush, *J. Ind. Eng. Chem.*, 1922, **14**, 1036.

[105] G.P. 353,744; *J.*, 1922, 754A.

[106] South Metropolitan Gas Co. and P. Parrish, E.P. 176,977; *J.*, 1922, 371A.

[107] *British Sulphate of Ammonia Federation, Ltd., Report*, 1922; *J.*, 1922, 514R.

[108] *Gas World*, 1922, **76**, *Cok. Sect.*, Mar. 4, p. 14.

[109] E.P. 179,723; *J.*, 1922, 501A; E.P. 173,818; *J.*, 1922, 173A. See *J.*, 1922, 733A.

The difficulty experienced in causing a washing liquid to penetrate a fine-grained salt while it is being centrifuged has caused the suggestion to be made that the acid salt should be mixed with mother liquor which has been specially purified and rendered alkaline with ammonia.[113]

It has been found that the alkaline washing liquid used for spraying the salt in the centrifuge can be replaced by a powder sprayed on the surface of the salt in the same way, and this lends itself to the production of a neutral salt with over 25·5% of ammonia without the employment of mechanical mixing machines or the application of external heat to dry the salt. Hence the natural grain of crystal is retained.[114]

R. Lessing finds it a good plan to prevent as much as possible cooling and crystallisation of the pasty salt while draining by lagging the draining vessel.[115]

Attention has been called to the advisability of removing phenols and similar objectionable substances before spent liquor is discharged, and a process has been tried, with some success,[116] which consists in passing furnace gases together with steam up through a tower-scrubber down which the spent liquor is caused to descend. The spent liquor is thereby rendered neutral or slightly acid and the phenols are expelled.

In view of the heavy cost of the acid used in making sulphate it has been proposed to manufacture the bicarbonate instead of the sulphate,[117] while the use of crude diluted ammoniacal liquor for direct application to the land is spreading on the Continent and excellent results are reported.[118]

[110] D. Thickins, and Ebbw Vale Steel, Iron and Coal Co., Ltd., E.P. 181,884; *J.*, 1922, 631A.

[111] Holmes & Co., Ltd., W. G. Adam, and C. Cooper, E.P. 187,035; *J.*, 1922, 982A.

[112] J. Marr, and Coke Oven Construction, Ltd., E.P. 187,320; *J.*, 1922, 982A.

[113] South Metropolitan Gas Co., E. V. Evans, P. Parrish, and O. Weight, E.P. 174,878; *J.*, 1922, 215A.

[114] G. Weyman, E.P. 183,089; *J.*, 1922, 669A.

[115] E.P. 178,046; *J.*, 1922, 414A.

[116] T. L. Bailey, *Alkali, etc. Inspector's Report*, 1921; *J.*, 1922, 317R. See also *Gas J.*, 1922, **159**, 213.

[117] W. Gluud, *Chem.-Zeit.*, 1922, **46**, 693, 715; *J.*, 1922, 722A, 399R. See also P. Rion, *Comptes rend.*, 1922, **175**, 172; *J.*, 1922, 856A.

[118] J. Mews, *Gas- u. Wasserfach*, 1922, **65**, 123; *J.*, 1922, 263A.

SULPHUR.

The examination of the various forms in which sulphur occurs in coal has been the object of several investigators with a view of reducing that portion of the sulphur which is left in the coke on carbonisation. F. Foerster and W. Geisler[119] assert that the hydrogen sulphide evolved on distillation almost entirely originates in pyrites. The ferrous sulphide first formed by thermal decomposition of the pyrites is decomposed by the joint action of hydrogen and steam. It is not considered practicable to eliminate the sulphur from coke without great loss of carbon. A. C. Monkhouse and J. W. Cobb[120] consider that the liberation of hydrogen sulphide follows the same lines as the liberation of ammonia, and they succeeded in obtaining 93·8% of the sulphur from the coke by heating to 1000° C. in presence of hydrogen and at lower temperatures in presence of steam. It is considered that the original nature of the coal affects the liberation of hydrogen sulphide.

On the other hand the work of J. P. Wibaut and A. Stoffel[121] tends to show that the sulphur originally present in inorganic form combines with carbon at high temperature to form very resistant compounds. It is concluded that washing the coal to remove pyrites may not alter the relative proportions of sulphur remaining in the coke to that evolved in distillation.

The removal of hydrogen sulphide from gas by liquid purification has been an attractive proposition not realised in practice.

F. W. Sperr[122] deals with the system elaborated by the Koppers Company in which a solution of sodium carbonate is used as reagent. The fouled solution is aerated and the residual liquor returned in cycle. Apparently, the gas has not been so far entirely freed from hydrogen sulphide by the process, nor has the sulphur removed from the gas been recovered, but possibly these objections may be met in the future.

E. V. Evans refers to the possible preferential combustion of the hydrogen sulphide,[123] but the formation of carbon oxysulphide has been a difficutly. With cold oxidants this would be avoided and possibly dye compounds may be of use in this direction.[124]

It has been suggested that the Claus kiln reaction, which is to all intents and purposes the normal purification process carried out at higher temperatures, can be so regulated by heating

[119] *Z. angew. Chem.*, 1922, **35**, 193 ; *J.*, 1922, 401A.

[120] *Loc. cit.*

[121] *Brennstoff-Chem.*, 1922, **3**, 273 ; *J.*, 1922, 888A. See also J. P. Wibaut, *Rec. Trav. Chim.*, 1922, **41**, 153 ; *J.*, 1922, 281A.

[122] *Gas World*, 1922, **76**, 334 ; *J.*, 1922, 359A ; E.P. 170,572.

[123] *Cf.* E. E. Naef, E.P. 172,074 ; *J.*, 1922, 58A. Also E.P. 170,152 ; *J.*, 1922, 167A ; E.P. 168,504 ; *J.*, 1921, 728A.

[124] *Gas J.*, 1922, **157**, 374.

elements dispersed through the material that while the sulphur liberated is carried forward and deposited separately to the purifying mass there is no trouble from formation of sulphur dioxide and similar compounds.[125]

It has been proposed to extract sulphur from spent oxide by a solution of ammonium sulphide.[126]

G. H. Gemmell deals with the question of valuation of oxide for purifying purposes.[127]

TOWN GAS.

The therm system of charging for gas has come under much ignorant criticism during the year, and as a result the Board of Trade has appointed a Committee of Inquiry into the matter. It seems to have been overlooked that many gas concerns were selling gas on a thermal basis (standard calorific value) several years before the therm was defined by the Fuel Research Board, and that this met with no serious objection.

The quality of gas to be "declared" naturally depends largely on the works manufacturing plant and other local conditions,[128] as well as on the relative values of coal, coke, oil, and various by-products. Most of the declared calorific values range from 450 to 500 B.Th.U., and there has been a tendency to increase the value to the latter figure, although G. Keillor[129] thinks that with a gas of 400–450 B.Th.U. the consumer is less likely to waste thermal value and therefore gains an advantage.

It is claimed by G. Helps[130] that low-grade gas (down to 250 B.Th.U.) can be distributed to give equal service at the same pressure as high-grade gas if the orifices of the burner nipples are enlarged approximately inversely as the decrease in calorific value. It would seem, however, that the increased internal resistance of the mains and services conveying larger volumes of gas must be overcome by some additional means.

Carbon monoxide.

The risks of carbon monoxide poisoning from coal gas are contrasted with other risks (tobacco smoking), which are cheerfully undertaken daily.[131] Investigation by Y. Henderson and colleagues into the physiological effects of carbon monoxide places a limit of danger to life when the time in hours during which inhalation takes place, multiplied by the concentration of carbon monoxide in parts per 10,000 is equal to 15. It is found that the best means of treatment for cases of such poisoning consists of inhalation of oxygen containing a small amount of carbon dioxide, the latter gas being effective in stimulating lung action.[132] The prominence given recently to the poisonous properties of coal gas has been followed by a large increase in the number of suicides accomplished by means of gas.

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[125] K. Cox, S. W. Kerr and E. J. Baty, E.P. 185,780; *J.*, 1922, 849A.

[126] Badische Anilin u. Soda Fabrik, E.P. 174,143; *J.*, 1922, 167A.

[127] *Gas J.*, 1922, **159**, 471; *J.*, 1922, 739A.

[128] G. M. Gill, *Gas J.*, 1922, **160**, 35.

[129] G. Keillor, *Gas J.*, 1922, **158**, 93.

[130] E.P. 184,820.

[131] E. V. Evans, *Gas J.*, 1922, **157**, 375.

CALORIMETERS.

A remarkably ingenious recording calorimeter has been devised by C. V. Boys[133] which is an outstanding example of a scientifically-designed instrument. The apparatus is of the water-flow type and includes, among other principles, the positive measurement of the water by a turn-over bucket system, and an adjustment of the gas rate, so that the temperature of the water is raised exactly 10° C., when the calorific value of the gas is of the "declared" value. There is also a "thinking machine," which contains a small ball-disc-cylinder integrator coupled with reduction gearing, which keeps the meter axle turning at a speed exactly proportional to the gas volume. The heat interchanger is of thin sheet lead, while the thermometers are filled with amyl alcohol. The record paper is ruled *in situ*, so that the ruled lines and record are always in proper relationship.

The Thomas calorimeter has been further developed.[134]

A new gas calorimeter is described by W. B. Davidson[135] in which the cooling water is introduced in a fine state of division in direct contact with the products of combustion.

The alteration in form and disappearance of the luminous tip of a gas flame by increase in aeration is the principle of two calorific value indicators.[136]

In another instrument the expansion of a liquid in the jacket of an explosion pipette caused by the heat of explosion of the gas is measured and compared with that resulting from the explosion of a gas of known calorific value.[137]

An instrument for regulating the flow of gas so as to compensate

[132] *J. Ind. Eng. Chem.*, 1922, **14**, 229; *J.*, 1922, 307A.

[133] E.P. 180,080; *J.*, 1922, 569A; *Gas J.*, 1922, **158**, 882; *J.*, 1922, 533A.

[134] E.P. 179,060, 182,573, 183,408, 183,409; *J.*, 1922, 485A, 731A.

[135] E.P. 171,246; *J.*, 1922, 38A.

[136] A. Grebel, *Gas J.*, 1922, **159**, 322; *J.*, 1922, 699A. See J. S. Withers E.P. 184,025; *J.*, 1922, 791A.

[137] Union Apparatebaugesellschaft m.b.h., E.P. 156,577; *Gas Engineer* 1922, **38**, 322.

for alteration in density is also described,[138] while a very useful paper on the various means of measuring the flow of gas is given by B. Dunglinson.[139]

Gas Analysis.

Little advance in method is to be found in gas analysis, attention having being chiefly directed to combining forms of existing apparatus such as that proposed by H. M. Lowe[140] and R. V. Wheeler.[141] E. W Blair and T. S. Wheeler, finding that the mercury lift in the Bone and Wheeler apparatus is tedious, use compressed air for altering the mercury levels in an elaborate modification of the apparatus.[142]

Some discussion has been aroused in respect to the determination of paraffins in coal gas. L. Levy describes combustion methods,[143] involving the use of a heated platinum wire. With such methods G. W. Jones and W. L. Parker[144] say that the platinum wire should not be heated above a bright yellow, and the time for combustion should not exceed three minutes, in which case the formation of nitrogen oxides does not exceed more than 0·003 c.c. The formation of the oxides of nitrogen is an error possible in explosion methods, but this may be disregarded when the explosive mixture is formed of air and the gas. Sparking the mixture does not cause the formation of nitrogen oxides.

J. C. King[145] adapts the Jaeger combustion method to the Bone and Wheeler apparatus, and after preferentially combusting the hydrogen and carbon monoxide explodes the paraffins with excess of air. By noting the amount of carbon dioxide produced and the oxygen used the mean composition of the paraffins can be calculated.

Processes of what may be styled physical analysis are being developed. The Shakespeare "Katharometer," in which the heat loss from a platinum wire is measured, has been applied to the determination of carbon dioxide and other gases.[146]

A method for continuously recording the carbon monoxide and dioxide in a gaseous mixture consists in mixing measured volumes of the gas with a liquid reagent and then measuring the change in electrolytic conductivity of the solution.[147] A simpler method takes notice of the change in colour of an indicator.[148]

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[138] South Metropolitan Gas Co., and D. Chandler, E.P. 176,524 ; *J.*, 1922, 353A.

[139] *Gas World*, 1922, **76**, *Cok. Sect.*, Jan. 7, p. 16.

[140] *Ibid.*, 1922, **76**, *Cok. Sect.*, Mar. 4, p. 19.

[141] *Gas J.*, 1922, **157**, 702.

[142] *J.*, 1922, 187T.

[143] *Gas Engineer*, 1922, **38**, 67.

[144] *J. Ind. Eng. Chem.*, 1921, **13**, 1154 ; *J.*, 1922, 159A.

[145] *Fuel*, 1922, **1**, 103 ; *J.*, 1922, 53A.

[146] See E.P. 124,453 ; *J.*, 1919, 393A ; E.P. 176,574 ; *J.*, 1922, 353A ; G.P. 346,682 ; *J.*, 1922, 353A.

COMBUSTION.

Further work has been carried out by W. Payman and R. V. Wheeler[149] on the combustion of complex gaseous mixtures which is discussed in relation to the composition and use of industrial gas.[150]

The flame temperatures of different gases are calculated by J. Brown[151] on the assumption of a specific heat for steam of 0·85 at 4000° C. In air the flame temperatures are given as hydrogen 2260° C., carbon monoxide 2400° C., methane 2070° C., and ethylene 2670° C. Methane is preferred for welding as its flame temperature is not high enough to injure metals operated upon.

Preliminary work of the Gas Investigation Committee of the Institution of Gas Engineers in regard to aeration of burners makes it difficult to lay down any definite relation between the various factors operating,[152] and does not confirm the conclusions of the American Bureau[153] when applied to the low velocities of air-gas mixtures usual in this country.

An interesting account of the development of gas burners is given by C. Carpenter,[154] who does not think that sufficient attention is given to the subject of gas lighting. Reference is made to experimental work of J. S. G. Thomas[155] on the effect on air entrainment of reducing the size of circular orifices for various pressures.

The efficiency of domestic water heating has been investigated by the U.S. Bureau of Standards,[156] who find that violent boiling of water in utensils with gas full on consumes nine times that necessary to maintain gentle boiling. When the lid is off five times as much gas is required as is necessary when the lid is on. When gas is consumed at the rate of 9000 B.Th.U. per hour the efficiency is practically constant with different gas qualities at

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[147] G. B. Taylor and H. S. Taylor, *J. Ind. Eng. Chem.*, 1922, **14**, 1008; *J.*, 1923, 76A.

[148] Victoria Falls and Transvaal Power Co., Ltd., and W. O. Andrews, E.P. 179,696 ; *J.*, 1922, 527A.

[149] *Chem. Soc. Trans.*, 1922, **121**, 363 ; *J.*, 1922, 359A.

[150] *Fuel*, 1922, **1**, 185; *J.*, 1923, 42A.

[151] *Z. angew. Chem.*, 1922, **35**, 328 ; *J.*, 1922, 577A.

[152] J. W. Cobb, *Gas J.*, 1922, **158**, 799.

[153] *Ann. Repts.*, 1921, **6**, 46 ; *J.*, 1922, 286A.

[154] *Gas J.*, 1922, **158**, 853 ; *J.*, 1922, 537A.

[155] *Phil. Mag.*, 1922, **44**, 969. *J.*

[156] *Gas J.*, 1922, **159**, 258, 530.

37%, and the time required to heat two quarts of water from 80° F. to boiling point is about ten minutes. The efficiency drops slightly with decrease in rate of gas supply and increases slightly with increased rate of supply.

The radiant efficiency of a modern gas-fire is about 50% of the net calorific value of the gas burnt.[157] W. A. Bone shows that the radiant efficiency is independent of the composition of the gas within wide limits and also of the calorific value, provided that the number of heat units developed per hour is kept suitably constant for the particular size of fire. Ventilation may be as good with a gas fire as with an open coal fire.

In respect of lighting A. R. Myhill[158] points out that it is inadvisable to test large lamps on a small-scale photometer.

It is thought that mantles impregnated with rare earths previously converted into fluorides by treatment with sodium or potassium fluoride give less shrinkage and a better efficiency.[159]

CORROSION.

The corrosion of cast-iron buried in the soil leaves as a residue a soft spongy mass mainly consisting of graphite, silica, and iron, retaining the shape of the original structure. Steel and wrought-iron, on the other hand, become pitted and the products of corrosion are carried away. Experiments have shown that magnesium salts are the most dangerous. The conclusion is reached that soil corrosion is an electro-chemical process depending chiefly on the composition of the metal, the nature of the soil, and the movement of the ground waters.[160]

The Life of Gas Meters Joint Committee review[161] recent changes of gas manufacture and their possible effect on internal corrosion of gas mains. The elimination of moisture below saturation point by further compression and cooling is discussed as the likeliest method of avoiding corrosion.

Interesting cases of corrosion of gasholder plates are noted by H. Tindale,[162] and the influence of unequal sun-heating in promoting corrosion by causing differences of electrical potential between various parts of the holder, is found to be an important factor. Probably, metal containing little or no manganese is to be preferred. Phosphorus appears to add to the resistance of the metal, but, on the whole, it is safer to use as pure and homogeneous a metal as possible.

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[157] *Brit. Assoc. Fuel Econ. Committee, 5th Report*; *J.*, 1922, 404R.

[158] *Gas J.*, 1922, **160**, 494.

[159] J. P. H. Soper, T. Terrell, and Terrell junr., E.P. 170,679; *J.*, 1921, 880A.

[160] J. W. Shipley, *J.*, 1922, 312A.

[161] *Gas J.*, 1922, **158**, 834; *J.*, 1922, 533A.

[162] *Ibid.*, 1922, **157**, 33.

Corrosion due to electrolysis by stray earth currents is dealt with in an interesting paper,[163] which also describes a method of detecting the source of the current from vibration sounds originating in the station generator and picked up by a telephone receiver.

TAR—TAR PRODUCTS.

Considerable attention has been given to the development of continuous tar distillation. The Hird tar plant and method of working are described by J. Curry.[164] About 5000 cub. ft. of gas (cal. val. = 450 B.Th.U.) is used for heating the stills per ton of tar distilled. Trouble in respect to chloride in the somewhat heavy tar used is overcome by washing the tar with hot water previous to distillation.

The somewhat sparse literature on tar distillation is enlarged by an interesting paper by E. V. Chambers[165] in which analyses of various descriptions of tars are given and some of the troubles in dealing with tar-liquor emulsions are described. In the new "cascade" type of continuous plant the main feature consists of a cascade or staircase arranged in the vapour space of the main still, down which the tar flows on entering the still and being dehydrated in a thin layer, local heating and frothing are avoided.

Another type of plant consists of a series of shallow stills with corrugated under-surface,[166] by which means, agitation, a large heating surface, and considerable strength are obtained.

J. L. Wilson[167] prefers to distil tar in the presence of an inert gas, separating the distillates by fractional condensation. The continuous distillation in fine films is provided for in a vertical vessel with a series of trays one above the other and inclined alternately from one side to the other, down which the tar falls in curtains against the ascending vapours.[168]

In another type of plant tar may be superheated under pressure in coils, so that on issuing from the coils with release of pressure the vapours are liberated and can be fractionally condensed. A series of such coils may be used and the pressures in the coils stepped down so as to obtain the usual fractions.[169]

Continuous steam distillation of tar is advocated by Ab-der-Halden,[170] particularly for small works. A plant for this purpose

[163] J. Chappuis and Hubert-Desprez, *Comptes rend.*, 1921, **173**, 1344.

[164] *Gas J.*, 1922, **158**, 149.

[165] *J.*, 1922, 178T.

[166] J. A. Yeadon, E.P. 183,682; *J.*, 1922, 703A.

[167] E.P. 180,347; *J.*, 1922, 538A.

[168] W. Glossop and L. Bradley, E.P. 184,242; *J.*, 1922, 743A.

[169] W. A. Walmsley, *J.*, 1922, 96T. See also *Gas J.*, 1922, **159**, 26

[170] *Chim. et Ind.*, 1922, 7, 226; *J.*, 1922, 286A. See E.P. 158,875; 1922, 457A; *Gas J.*, 1922, **160**, 107.

consists of a filter and settling tank from which the tar gravitates to a dehydrator in which it is heated by the products of distillation from the still proper. The dehydrated tar flows down a column provided with packing into the still proper, where it is distilled with superheated steam supplemented by direct firing. By filtering the tar through a filter having a mesh equal to half the area of the inlet orifice which regulates the feed, the plant can be made largely automatic.

S. A. Wikner[171] finds that continuous distillation is to be preferred for the preparation of road tars, which are prepared by distilling tar almost entirely to pitch, the fractions afterwards being mixed to conform to specification. A special dehydration arrangement is described, in which tar is heated both by the distillation products from the stills proper, and by additional closed steam coils. As the dehydration is the major part of the work to be done, a greater throughput is obtained, and it is claimed that only 40 lb. of breeze is required to dehydrate one ton of tar.

Other means of imparting heat to tar may be used. In one case the mixture of oil and water (or tar) is injected into a previously dehydrated portion of the oil heated to a temperature above the vaporising point of water or lower oil fraction, the steam and vapours afterwards being separated in an expansion chamber.[172] Or the tar may be sprayed or forced through a jet into a bath of molten metal, say at 400°–500° C. at a pressure of 50–60 atmospheres, contained in an autoclave. Metals which will combine with sulphur may be used so as to eliminate sulphur from the distillation products.[173] Or, the tar may be passed below the surface of molten metal in one or more vessels at the same or different temperatures, by being carried under the surface on a revolving drum.[174]

Tar Products.

The use of prepared tar for road purposes has greatly extended, and sometimes it has been found advantageous to mix a certain amount of bitumen with the tar. The possibility of fish poisoning taking place through river water becoming contaminated by road drainage has caused discussion. W. Kirby[175] refers to the similarity of the fish poisoning from tarry water to the "pitch cancer" of pitch workers. This latter is supposed to be due to the presence of acridine. As blast-furnace pitch is free from this objection it is suggested that it might be used for road purposes in the neighbourhood of fish-preserving waters. Methods of estimating tar acids and bases in road drainage and mud are described.[176]

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[171] *Gas J.*, 1922, **158**, 319; *J.*, 1922, 457A.

[172] Asiatic Petroleum Co., Ltd., and W. Cameron, E.P. 173,644; *J.*, 1922, 131A.

[173] E. Blümner, G.P. 338,846; *J.*, 1922, 496A; E.P. 182,868; *J.*, 1922, 407A.

[174] Thermal Industrial and Chemical Research Co., A. McD. Duckham, and J. S. Morgan, E.P. 174,690, 174,974, 176,438; *J.*, 1922, 240A, 315A. See also E.P. 184,624; *J.*, 1922, 803A.

[175] *J.*, 1922, 218R.

The results of an elaborate survey of the properties and products of distillation of low-temperature tar (produced from the "Carbocoal" process) are given by J. J. Morgan and R. P. Soule,[177] and the characteristics of coke-oven, gasworks, and the low-temperature tars in question are contrasted. The preponderance of cyclic compounds in the latter suggests that coal itself may possess a "cyclic" structure.

H. Moore describes the effect of impurities in oils prepared for use in Diesel engines and enumerates the methods of examination necessary for the selection of such oils.[178]

Further methods of preparing lubricating oils from tar, particularly from low-temperature tar, have been suggested. In one, the tar oils are passed with about an equal weight of superheated steam at 300°–400° C. through a tube with a flattened constricted portion heated to 500°–900° C., so that the oil is in the heated area not more than 30 seconds.[179] In another process the oil, after removal of acid constituents is treated simultaneously with liquid sulphur dioxide, and a hydrocarbon insoluble in sulphur dioxide.[180] Phenols, which are objectionable in connexion with the preparation of lubricating oil, may be converted into esters by reaction with β-naphthalenesulphonic acid.[181]

Continuous benzol washing is proposed in a process which consists of spraying the benzol at high pressure through the acid in a special apparatus.[182] Dilute acid at a suitable temperature is said to polymerise foreign matter in benzene to high-boiling substances, which may be recovered and used as varnish.[183]

Cases of benzol poisoning are not unknown, and are commented upon by C. H. Horan,[184] who points out the inadvisability of employing workmen already in a debilitated condition.

Phenol of a permanent pale yellow colour is said to be obtained by treatment with hot concentrated solutions of sodium bisulphate and thiosulphate,[185] while sodium sulphide solution has been used for dissolving the more strongly acid phenols such as the cresols and xylenols from tar oil.[186]

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[176] J. J. Fox and A. J. H. Gauge, *J.*, 1922, 173T.

[177] J. J. Morgan and R. P. Soule, *Chem. and Met. Eng.*, 1922, **26**, 923, 977, 1025; *J.*, 1922, 491A, 495A.

[178] *J.*, 1922, 319A.

[179] H. O. Traun's Forschungslaboratorium G.m.b.H., E.P. 156,140; *J.*, 1922, 404A.

[180] Allgem. Ges. für Chem. Ind. m.b.H., G.P. 341,872; *J.*, 1922, 48A.

[181] M. Jacobson, *Brennstoff-Chem.*, 1922, **3**, 10; *J.*, 1922, 134A.

[182] R. Mezger, *Gas u. Wasserfach*, 1921, **64**, 825; *J.*, 1922, 49A.

[183] J. Demant, E.P. 179,610; *J.*, 1922, 539A.

[184] *Chem. and Met. Eng.*, 1922, **27**, 605.

[185] M. Pfautsch, G.P. 341,231; *J.*, 1922, 93A.

The *m*- and *p*-cresols in crude tar acids may be separated by taking advantage of the difference in the rates of sulphonation.[187] Phenol in tar acids may be estimated by a method involving the determination of the freezing point of the hydrate.[188]

The production of indene is described.[189] The coal tar fraction of boiling point 175°–185° C., after the separation of phenols and bases, is heated with caustic potash at a temperature above 170°–180° C. for two or three hours in a closed vessel. The potassium-indene compound is separated from oil, decomposed with water, and the crude product afterwards purified.

A method of estimating phenanthrene suitable for mixtures containing 30% or more of phenanthrene and not more than 10% of carbazole is described.[190]

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[186] F. Fischer, H. Tropsch, and P. K. Breuer, *Brennstoff-Chem.*, 1922, **3,** 1; *J.*, 1922, 134A.

[187] A. F. Campbell, *J. Ind. Eng. Chem.*, 1922, **14**, 732; *J.*, 1922, 661A.

[188] W. H. Hoffert, *J.*, 1922, 334T.

[189] R. Weissgerber, G.P. 345,867; *J.*, 1922, 407A.

[190] A. G. Williams, *J. Amer. Chem. Soc.*, 1921, **43**, 1911; *J.*, 1922, 49A.

MINERAL OILS.

By J. E. Hackford,

Chemical Adviser to H.M. Petroleum Department.

The year 1922, taken as a whole, has not proved to be a very happy one for the petroleum industry, for, as was to be expected, the full weight of the trade depression following the war has been experienced. Again, political conditions of the day are not conducive to speedy progress, especially with regard to the petroleum industry. To-day, the general policy appears to be "grab oil-land," and this policy is affecting all nations at the present moment, and the clashing of the various national interests is still the cause of unrest.

The value of liquid fuel for transport purposes was realised by all and sundry during the war, and the lesson is firmly implanted in the mind of even the lowest in the land. The Fifth Report of the British Association Fuel Economy Committee draws attention to the fact that the total crude oil produced in England for the year 1920 amounted to no more than 227,200 tons. The Report states: "The Committee considers it important that attention should be drawn to the fact that, inasmuch as the home production of shale oil is practically negligible, owing to the relatively low cost of production of imported petroleum, we are at present dependent almost entirely on countries outside the Empire for our supplies of natural petroleum and petroleum products, a most undesirable and dangerous state of affairs from every point of view." It is also pointed out that the output of coal in Great Britain during the year ending December 31st, 1921, fell to 163 million tons, the imports of oil into Great Britain amounting to four and a half million tons. As our domestic requirements of coal amount to 50 million tons per annum, it will be seen that even the supply of imported mineral oils is relatively small for power production.

It is now realised that it is very necessary to increase the available home supplies of petroleum, and also the supplies within the British Empire itself. The British peoples are not unique in having adopted the view that they must have available and ready supplies of petroleum products in case of need. Other nations have done the same, but work has been delayed in the various countries owing to the unsettled conditions; there is little doubt, however, that as soon as these conditions become more stable, the oil industry will be one of the first to revive.

The achievements of the engineering world have also had an appreciable effect on the position of the oil industry. Low-compression internal-combustion engines are rapidly approaching a state of perfection, and the increasing demand for them causes a correspondingly increasing demand for motor spirits. A year or two back, the whole industry was agape with the pessimistic indications that the available supplies of mineral oil would soon be exhausted. To-day we find that the United States is curtailing her production of crude oil on account of this phenomenal demand for motor spirits, for even there the demand for motor spirits exceeds the supply. Consequently, the outlook for those nations that depend upon supplies imported from that country is not encouraging. The United States are producing 570 million gallons per month, and are using 580 million gallons per month.

The result of this state of affairs is to encourage "cracking processes" on the one hand, whilst, on the other hand, in order to utilise economically all the crude treated, the heavy residues must be sold. The demand for these is far less than the now available supplies, and the consequence is that manufacturers have to dispose of them at a loss, or at barely paying prices.

The French Government have offered prizes for a motor fuel which shall not consist entirely of petroleum products, and the last year has seen much valuable work carried out in this respect. This "National motor fuel," as it is known, consists of a mixture of petrol and alcohol, together with a small percentage of some particular solvent to ensure complete miscibility. So far, experience has shown that small quantities of cresols, cyclohexanol, isopropyl and butyl alcohols answer this purpose, and prevent, or at least diminish, the tendency of the petrol and alcohol to separate into two distinct layers. The performance of this "National motor fuel" is said to be good in practice. Trials showed that, without the slightest modification of the engine or carburettor, a fuel composed of petrol with 10–20% by vol. of 95% alcohol, could be used. With this proportion, the power remains roughly constant; further addition of alcohol leads to a diminution of power if the engine conditions are not modified.

Oil was struck at the D'Arcy well, near Edinburgh, on May 6th, 1922. J. E. Hackford[1] gives an analysis of the oil, and emphasises its significance, pointing out the unusual circumstance of a well being drilled in the midst of a shale field, and comments upon the conditions which led to a prognosis of the quality of the oil in 1915, and the outstanding fact that the oil is substantially similar in quality to that obtained at Hardstoft. This is illustrative of the fact this class of oil persists throughout Great Britain.

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[1] *J.*, 1922, 245R.

ORIGIN OF PETROLEUM.

Very little has been added to our knowedge of this subject. R. E. Somers[2] suggests that the lighter fractions are added to the first light-formed crude oil owing to increased pressure and the effect of lengthy periods of time. C. C. Rae[3] suggests that humic acids and associated organic compounds are the intermediate step between the crude petroleum oils and complex plant compounds, and in evidence of this theory is quoted the observation of Binney, that petroleum was formed by the decomposition of peat mosses, at Down Holland in England, in the presence of infiltered sea-water. Haseman, it is stated, and others have also noted the association of swampy areas near the sea with asphalt and other hydrocarbons. There seems to be some relation between the humic acid and silica content of river waters, probably in some way connected with their colloidal nature, but, on admixture with sea-water, organic compounds are deposited, owing to coagulation by electrolytes. It would also appear that silica is deposited at the same time, judging from the presence of finely-divided silica in Californian shales, associated with petroleum. The humic acid carried by rivers every year totals several millions of tons, and the gradual transformation of this into petroleum hydrocarbons probably occurs under several different conditions, in which pressure, temperature, alkalinity, salts, and the presence of catalytic agents all vary. In the western parts of the United States are found oil shales containing organic compounds intermediate between humic acids and petroleum, which are convertible into the latter by means of heat. Fairchild[4] suggests that a vast amount of hydrocarbons may have been held in strata, now below the observable rocks, and these have been forced up to form reservoirs of volcanic emanations.

K. Kobayashi[5] is attracting more and more attention to his theory of the fish-oil origin of petroleum. The reasons of his conclusion that petroleum was prepared from fish-oil by dry distillation with acid-clay are: (1) Topographical relationship exists between the distribution of Japanese petroleum and acid-clay. (2) The petroleum is mostly found mixed with sea-water. (3) Acid-clay and neutral salts when heated together form free acids. (4) Certain fish-oils contain free hydrocarbons (*e.g.*, squalene). His paper gives experimental details, with figures, showing the relationship between the artificial and the natural benzines and kerosenes from which is deduced the theory of the marine-animal origin of Japanese petroleum.

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[2] Amer. Chem. Soc., Pittsburgh Meeting, Sept., 1922.

[3] *Trans. Amer. Inst. Min. Met. Eng.*, 1922, No. 1137-P, 4 pp.

[4] *Oil and Gas J.*, No. 61, 70.

[5] *J. Chem. Ind. Japan*, 1921, **24**, 1; *J.*, 1921, 250A.

J. E. Hackford[6] makes out a case for the derivation of Mexican petroleum from seaweed. He points out that the outstanding features of Mexican petroleum are, high sulphur content, aliphatic nature, minute nitrogen content, low-content of aromatics, and multiplicity of elements present in the ash of the oil. There is ample sulphur in the alga *Macrocystis pyrifera,* which is present in abundance in the Gulf of Mexico. Algæ contain little or no nitrogen. The fact that aromatic hydrocarbons are practically absent in the oil may be accounted for by the absence of cellulose in the algæ. The presence of numerous elements in the ash of the oil also bears out this view. He also puts forward a new theory to interpret the significance of the different qualities of gases derived from oils.

NOMENCLATURE.

The same author strongly pleads for a chemical classification of oils to supplant those existing classifications which are based upon the physical properties of oils and their derivatives.[7] All mineral oils contain aliphatic hydrocarbons, and, in consequence, the nomenclature is based upon the fraction of the oil present, which forms its distinguishing characteristics. The oils are divided into the following classes: (1) Aliphatic oils. (2) Aromatic oils. (3) Naphthenic oils. (4) Naphthylenic oils. Each of these may contain the oxygen or sulphur derivatives. For example, an aliphatic oil is a mixture of aliphatic hydrocarbons, either saturated or unsaturated, and may contain their oxy- or thio-alcohols and/or ethers—*e.g.*, oxy-aliphatic oil (Pennsylvanian), thio-aliphatic oil (Mexican). Other examples are given.

The solid bitumens are all covered by the term "petrolite." If soluble in carbon bisulphide, they are called "asphaltites," and if insoluble, "kerites." Thus, "Wurtzilite" is insoluble in carbon bisulphide, it contains a large percentage of sulphur, and is derived from an aliphatic oil. According to this chemical classification, it would be called a thio-aliphatic kerite.

Under this sub-heading may be mentioned the growing cry for economy in oil-fields. The criminal waste that daily goes on by the owners failing to drain their wells, failing to prevent water intrusion and the subsequent carrying-away of the oil, and the economic loss to the nations by their failing to use their gaseous products, are being more and more realised. Methods are now being devised to overcome the oil losses, such as in the utilisation of compressed air, of vacuum, and of scientifically washing oil-sands with water. In this respect the paper by A. B. Thompson[8] is instructive. He points out the evil effects of competitive drilling on leases of restricted dimensions, and the paper, in general, is a great asset to the present-day literature upon this subject; he is ably supported by A. F. Dabell,[9] and it is hoped that this branch of the science of oil-winning will receive increasing attention.

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[6] *J. Inst. Pet. Tech.*, 1922, **8**, 193; *J.*, 1922, 401A.

[7] *Ibid.*, 1922, **8**, 193.

TREATMENT OF CRUDE OILS.

There has been no striking feature brought to light during the last year. The general lines that have been pursued are the development of the tubular and pipe still type of retort, not only for distillation purposes, but also as a means of reducing the viscosity of heavy crude oils and residuals. A. E. Dunstan and F. B. Thole[10] suggest treating the crude and residual oils at a temperature of 400° C. and at the high pressure of 200 lb. D. Pyzel, whose name must be associated with that of Trumble, continues to patent improvements in heat-exchanging devices for the purpose of re-running distillates by means of the heat contained in the heavy hot residues of the crude oil.[11] Another process for lowering the viscosity of crude oils has been patented by R. H. Brownlee and C. F. de Ganahl.[12] It is virtually the same as the above, but with the suggested use of catalysts, such as nickel, iron, etc.

L. A. Mekler,[13] in a most instructive paper, says that, in the refining of petroleum, the fuel bill is one of the main items of production costs, yet, with most stills, the thermal efficiency is around 26%, compared with 75% to 80% in the modern steam boiler. The working range of a still with pre-heaters incorporated is between 150° and 450° F., but boiler design cannot be entirely successfully applied, owing to the great difference in specific heat and chemical constitution between oil and water. The first requirement of a still is the "gradual bringing up of the whole body of the oil to the desired temperature at a rate that does not exceed the thermal capacity of the oil, and the heating conductivity of the container." Counter-current heating is 42% more efficient than concurrent and avoids local over-heating. Capacity is increased by using small tubes and a large volume of low-temperature gases. A coil-still with over-fired furnace is superior to a header still in supplying these requirements. The proper mixing of the combustion gases in the furnace is of the greatest importance. The best burners for gas and gasified oil have a coefficient of 0·9–0·95, whilst atomising oil burners (low compression) seldom exceed 0·8, and high-pressure ones still less. Nozzle velocity should just exceed the velocity of the propagation of flame of the particular fuel used, and complete combustion should have taken place before the gases enter the heating zone. The design of the combustion chamber is of the greatest importance, and for each temperature there is a fixed ratio between the combustion space and the amount of fuel burned, almost independent of the character of the latter. The circulation of the burnt gases is also very useful in producing even heating.

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[8] *Ibid.*, 1922, **8**, 1.

[9] *Ibid.*, 1922, **8**, 50.

[10] E.P. 156,284; *J.*, 1922, 537A.

[11] U.S.P. 1,383,024; *J.*, 1921, 568A.

[12] E.P. 177,589; *J.*, 1922, 404A.

[13] *Chem. and Met. Eng.*, 1922, **26**, 774.

W. A. Brown[14] has patented a process for dehydrating oils. This process consists in heating the mixture under pressure sufficient to prevent the vaporisation of the water, and thereby inducing the separation of the oil.

DESULPHURISING PROCESSES.

J. C. Clancy has patented a process[15] in which the oil is treated with liquid anhydrous ammonia, to cause the formation of an ammonia-sulphur compound, which is then separated. A catalyst may be used to cause the sulphur to combine with the ammonia. A. C. Nesfield[16] introduces a new method in which oil is treated with a thin film of chlorine gas. The treatment takes place in a tower, down which the oil descends, being caused to form films by flowing over cones. The chlorine is circulated, but has to be replaced in time, owing to loss of efficiency. The sulphur is precipitated in flocculent form, and is separated from the oil by filtration or centrifugal treatment, or removed by means of water. The reaction is expedited by the addition of quicklime, and by pre-heating the oil to a suitable temperature. The precipitate consists of sulphur compounds in addition to sulphur, and may contain bituminous matter.

E. B. Cobb[17] removes elementary sulphur from petroleum oils by means of monosulphides of alkali or alkaline-earth metals, which combine with the sulphur to form alkali polysulphides.

Whilst dealing with desulphurising processes, it would be well to record the results of the experiments carried out on engines using fuels with a high sulphur content. These experiments were conducted by Professor G. Winchester for the Standard Oil Company of New Jersey. A Hvid type of Diesel engine (Thermoil) was used. Several fuels were tested to ascertain the effects of both free and organic sulphur. The runs were continued for 384 hours. The fuels included high-sulphur Mexican crude and gas-oil, and mixtures of these with a polymer oil containing about 19% of combined sulphur, or 10% of sulphur in the mixed fuel.

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[14] U.S.P. 1,419,610 ; *J.*, 1922, 580A.

[15] U.S.P. 1,423,710 ; *J.*, 1922, 701A.

[16] E.P. 183,527 ; *J.*, 1922, 701A.

[17] U.S.P. 1,413,005 ; *J.*, 1922, 404A.

The running time for these fuels was about 180 hours, and the compression in the engine reached 500 lb. A run of 204 hours' duration was made with kerosene containing 0·85% of free sulphur in solution. Further examinations of the dismantled engine disclosed no evidences of corrosion, nor was the copper tubing appreciably affected. Trouble was encountered by the excessive formation of carbon which deposited on the exhaust valve, and clogged the spray-holes to the cylinders.

OTHER PROCESSES AFFECTING CRUDE PETROLEUM OILS.

Mention must here be made of the Bergius process[18] which is one of the most important of recent discoveries. It consists in heating powdered coal with petroleum or tar-oil for about six hours at a temperature of 400° C. in the presence of hydrogen under, approximately, 100 atmospheres pressure. It is claimed that 87% of the coal is converted into liquid products under special conditions. F. Fischer and H. Schrader[19] have also described a method of producing hydrocarbons from coal by heating it with a mixture of carbon monoxide and steam at high temperatures and pressures.

CRACKING PROCESSES.

There is a tendency for these processes to fall under two headings—these which have as their object the cracking of heavy crude oils or heavy crude residues, with the object of lowering the viscosity, in order to make them into more merchantable fuel oils, and secondly, those processes which aim to produce gasoline from heavy distillates. The commercial conditions of the past year have encouraged work on the former processes, for keen rivalry and competition have forced vendors to resort to them.

The usual method employed is to pump the oil at a pressure of 200–500 lb. through a tubular still at a temperature of 400°–500° C. The viscosity of an asphaltic oil is greatly reduced by such treatment.

W. M. McComb[20] passes a mixture of steam and oil through a tube heated in such a manner that the temperature at the oil inlet is equal to the initial, and at the outlet to the final boiling point of the oil. The increase in temperature from one end to the other of the tube corresponds with a fractional distillation of the oil. This treatment is said to produce very little fixed gas and carbon. E. M. Clark[21] passes the ingoing oil through the vapour pipe, between the condenser and the still. J. H. Adams[22] places a solid cylinder, of a diameter almost equal to the still tubes, in the tubes themselves. These cylinders are constructed to carry a helical scraper to remove the carbon deposit. J. W. Coast[23] cracks the low-boiling oils at high temperatures and pressures, and, without cooling, forces the vapours into high-boiling oil which is then distilled at lower temperatures and pressures. F. B. Lewis and T. S. Cooke[24] have a process by which the cracked vapours are passed through petroleum oil maintained at such a temperature that the uncracked fractions are condensed, whilst the cracked products distil over. The use of molten metals still finds favour in the eyes of investigators, and A. J. Paris[25] passes the oil through molten metal, after which operation the products are compressed and condensed.

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[18] F. Bergius, E.P. 148,436 ; *J.*, 1921, 838A.

[19] *Brennstoff-Chem.*, 1921, 2, 257; *J.*, 1921, 683A.

[20] U.S.P. 1,374,858 ; *J.*, 1921, 379A.

One of the outstanding difficulties of cracking processes lies in the removal of the carbon deposited in the cracking tubes or stills during the operation. Helical scrapers, stirring rods, and other devices have been suggested, but latterly there has been a deal of work done in attempting to remove this by means of moving heavy iron balls. As an example of this method, R. H. Brownlee and C. F. de Ganahl[26] heat the oil to the required temperature in a still or series of stills, consisting of a revolving drum containing a number of metal balls. These may be of iron or steel, or of some metal possessing catalytic properties, and should be hollow, to give the necessary surface without unnecessary weight. Their action is to increase the heating surface, and also to effect a pulverising action on the residue as it becomes solid. Another method of overcoming this difficulty has been patented by F. E. Dodge[27] who takes care that the carbon is deposited in a place where it can do no harm. Solvent naphtha or other high-boiling aromatic hydrocarbons are introduced into a coking-oven after all oil and gas has been distilled off from the coal, whilst the coke is still at a temperature of 600°–800° C. The products of cracking are condensed and separated in the usual way, and unconverted portions returned to be re-cracked. The carbon formed during the reaction is deposited on the coke itself. By this means the use of special apparatus and auxiliary heating is rendered unnecessary.

[21] U.S.P. 1,388,514 ; *J.*, 1921, 728A.
[22] E.P. 141,689 ; *J.*, 1921, 804A.
[23] U.S.P. 1,388,629 ; *J.*, 1921, 728A.
[24] U.S.P. 1,392,584 ; *J.*, 1921, 804A.
[25] U.S.P. 1,392,788 ; *J.*, 1921, 804A.
[26] E.P. 173,242 ; *J.*, 1922, 131A.
[27] U.S.P. 1,409,893 ; *J.*, 1922, 322A.

MOTOR SPIRIT.

The subject of the physical properties of motor fuels has received the attention of W. R. Ormandy and E. C. Craven.[28] The following properties are thoroughly investigated: Heat of combustion, freezing point, separation point, distillation point, latent heat of evaporation, flash point, explosive range, corrosiveness, viscosity, toluene number, spontaneous ignition temperature. This paper is of the utmost importance, and, concurrently, should be read T. Midgely and T. A. Boyd's review of the chemical control of gaseous detonation, with particular reference to the internal-combustion engine.[29] This subject is of increasing importance. The addition of such substances as diethyl selenide, or lead tetraethyl, when present in as little as 1 in 200,000 parts of fuel mixture, prevents "knocking" in an engine. The preventive effect does not increase indefinitely in proportion to the amount of "anti-knock" material present, but tends towards a maximum. By retarding the velocity of combustion it tends to insure its completeness, and thus increases the efficiency of the fuel. Unlike ordinary catalysts, these negative ones are themselves destroyed in the reaction, being, for the most part, combustible materials.

Interesting work had been carried out by G. G. Brown,[30] who describes how by properly controlling the air and fuel mixture of an engine, the efficiency may be raised to between 30% and 35%. G. W. Jones and A. C. Fieldner[31] claim that considerable fuel economy can be effected by the analysis of the exhaust gas, in controlling carburettor setting. An increase in mileage of 20% on American Government trucks was effected by this method. The average of several thousand analyses from 101 cars showed 70% combustion. Brown states that "the combustion or explosion of a gasoline air mixture is essentially a complex chemical reaction, and, as such, is susceptible to chemical control. The most important consideration is the velocity of reaction, which is determined by concentration, turbulence and temperature."

In the refining of motor spirits, a new process has been patented by A. E. Dunstan.[32] He finds that, by treating liquid hydrocarbon oils with an alkali hypochlorite solution, the bulk of the sulphur compounds are removed. The same process is recommended by H. W. Young and A. W. Peake.[33]

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[28] Inst. Auto. Eng., Feb., 1922.

[29] *J. Ind. Chem. Eng.*, 1922, **14**, 894; *Nat. Petr. News*, 1922, **14**, 59.

[30] *J. Ind. Eng. Chem.*, 1922, **14**, 6[illegible]; *J.*, 1922, 279A.

[31] *Chem. and Met. Eng.*, 1922, **27**, 590; *J. Ind. Eng. Chem.*, 1922, **14**, 594; *J.*, 1922, 622A.

[32] E.P. 184,281; *J.*, 1922, 741A.

[33] *Chem. and Met. Eng.*, 1922, **27**, 972; *J.*, 1923, 43A.

Silica gels, bauxite, and activated charcoal are increasing in popularity as deodorising and decolorising agents for motor spirits and other distillates. In this respect the work of A. E. Dunstan and F. B. Thole,[34] and of L. W. Parsons and L. R. Churchill,[35] is noteworthy.

J. C. Morrell and G. Egloff[36] discuss the refining of cracked distillates, whilst the degree of unsaturation and the methods of estimating this are discussed in a very able paper by E. M. Johansen.[37] The same subject-matter also receives the attention of W. F. Faragher, W. A. Gruse, and F. H. Garner.[38]

LUBRICATING OILS.

The question of the causes that contribute towards an efficient lubricant has received quite a little attention during the past year. L. Archbutt[39] reviews the theory of viscous lubrication, and, incidentally, strongly advocates the use of the poise. It is of interest to note that the effect of pressure on the viscosity of oils is much greater in the case of mineral oils than with vegetable oils—*e.g.*, at 6·5 tons to the square inch Mobil Oil B.B. increased in viscosity in ratio of 27 to 1, while castor-oil only increased 4·5 to 1. It is important to note the effect of crystalline paraffin wax on the viscosity of lubricating oil; E. W. Dean and L. E. Jackson[40] state that changes up to 90% in the paraffin wax content of Pennsylvania lubricating oils have a negligible effect on the viscosity through a considerable range of temperature.

The methods of measuring the property of oiliness are discussed by R. E. Wilson and D. P. Barnard,[41] who, as a result of experiments, believe that the static friction test is the best single test of the property of oiliness.

An important discovery has been made by H. M. Wells and J. E. Southcombe[42] who found that, by the addition of small quantities of certain organic acids and bases, the viscosity of a lubricating oil is greatly increased. Another commercial advance with regard to lubricating oils lies in the increasing use of the centrifuge for the separation of water and waxes. P. T. Sharples' method[43] may be here mentioned. Straight or diluted wax distillates are first chilled, and then submitted to centrifugal treatment, adapted so that the wax and wax-free residues are continually discharged.

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[34] E.P. 186,955; *J.*, 1922, 975A.

[35] *Chem. and Met. Eng.*, 1922, **27**, 590.

[36] *J. Inst. Pet. Tech.*, 1922, **8**, 540.

[37] *J. Ind. Eng. Chem.*, 1922, **14**, 288; *J.*, 1922, 402A.

[38] *Ibid* 1921, **13**, 1044; *J.*, 1922, 90A.

[39] *J.*, 1922, 287T.

[40] *U.S. Bureau of Mines, Reports of Investigations, No.* 2249.

[41] *J. Ind. Eng. Chem.*, 1922, **14**, 683; *J.*, 1922, 929A.

[42] E.P. 168,076; *J.*, 1921, 728A; *cf. J.*, 1920, 51T.

[43] U.S.P. 1,416,890; *J.*, 1922, 536A.

Whilst there have been quite a number of papers and articles relating to the oxidation of oils, and to the separation of aldehydes and acids therefrom, nothing has transpired which calls for special attention.

COLOURING MATTERS AND DYES.

By E. Arthur Bearder,

Dyestuffs Adviser, Association of British Chemical Manufacturers.

It has been freely stated that Germany's former world supremacy in the synthetic dyestuff industry was attributable to three main factors, namely, her splendid organisation, technical experience of organic chemical manufacture, and peculiar scientific ability or aptitude. To-day the mass of opinion in this country inclines to the view that the British chemical brain is at least equal to the German in power of conception and in application. Steadily, since the world-war gave the great impetus to our organic chemical enterprise, we have been building up experience in applying scientific facts and discoveries to the manufacture of industrial commodities—intermediates and dyestuffs. But perhaps our greatest advance is marked in the corporate existence of the branches of our chemical manufacturing concerns in the strong organisation known as the Association of British Chemical Manufacturers, which came into being in 1916. The Association is divided into groups, one of which comprises practically all the dyestuff and intermediate manufacturers in the United Kingdom. A representative Committee of this Group constitutes an active body, which meets regularly to discuss, for the common good, problems connected with its branch of the industry. It is, in effect, to the dyestuff manufacturers what the Colour Users' Association is to the consumers of dyestuffs. Both Associations are represented on the Dyestuffs Advisory Licensing Committee (Import Regulation) and the Dyestuffs Industry Development Committee of the Board of Trade, and a joint committee of technical representatives of each body is now in existence for the purpose of rendering mutual assistance in technical problems appertaining to the requirements of the dye-using and dye-making sections of the community.

The Dyestuffs Advisory Licensing Committee appointed by the Board of Trade, consequent upon the passing of the Dyestuffs (Import Regulation) Act, in December of 1920, is completing its second year of service. Born in strife, it has lived through two turbulent years, weathering a storm of political and public criticism in a manner that speaks well for the high ideals of public service which have actuated its members, the majority of whom represent factions whose immediate interests are diametrically opposed. The volume of work discharged by this Committee will be appreciated when it is understood that not a single synthetic dyestuff or intermediate product can be imported into the country without a recommendation from the Committee, and that every individual application for a licence to import is carefully examined and adjudicated upon by the Committee. Political considerations apart, it may be taken that this body has lived down adverse criticism, and that in its place there is the realisation that the duty of ensuring an adequate supply of dyestuffs to the user, simultaneously with protection of the interests of the colour maker, is being successfully discharged. However, the present economic position is an extraordinarily difficult one, and competition in price of dyewares is bound to place the British manufacturer at a disadvantage so long as the value of the German mark remains at a low level of depreciation.

The past year bears undoubted traces of the determination with which Britain is tackling the work of the building up an efficient dyestuff industry. Our universities and factories have conducted no mean volume of research, to which the scientific and patent literature bear witness. Wide fields of investigation have been explored and numerous improvements in existing, and achievement of new, processes recorded. Valuable work upon the molecular configurations of adjective dyestuffs, and the nature of their combinations with metallic mordants, continues, and further important contributions to our knowledge of this subject have been published.[1] Much interest has been aroused by the publication of the results of an investigation carried out by British researchers bearing upon the relation between the chemical constitution and antiseptic action of coal tar dyestuffs.[2]

Mention should be made of a literary contribution of some magnitude which is in process of compilation under the auspices of the Society of Dyers and Colourists. The "Colour Index," as it is styled, is a work of reference on the lines of the old—and now somewhat out-of-date—German "Farbstofftabellen" of Schultz and Julius, and when completed, will be a thoroughly up-to-date compendium of information on dyestuffs, designed to supply a long-felt want to colour manufacturers, users, and students —the colourists of the future

The primary object of these efforts is the production of dyestuffs, and it will be conceded that, in spite of many serious set-backs, such as financial stress and trade depression, real progress has been made during the year under review. Colours already in manufacture have been improved in quality to meet the demands of the consumer, who, quite justifiably, expects to be supplied with products which will enable him to hold his own in competition with his foreign competitors. This type of advance on the part of the dye maker is not always accorded the appreciation that it deserves, for it often represents a form of progress which, like experience, only comes with time or rather, perhaps, with opportunity to practise processes involved. At the same time one would wish to place on record the very earnest desire evinced by the consumer, in general, to avoid excess in his demands in this respect, and to afford facility for the attainment of the desired result. If it cannot be claimed that many entirely new colours have been turned out, it must be remembered that the actual demands of the dyer and printer have to receive first consideration, and these have, naturally, been for commodities already tried, approved and used. Thus it follows that for some time the British dye maker will be principally occupied in consummating the manufacture of colours which were hitherto the monopoly of foreign firms—often an extremely difficult and laborious process. In pursuance of this policy a considerable number of new and important members have been added during the year to the existing comprehensive range of British colours.

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[1] G. T. Morgan and collaborators, *Chem. Soc. Trans.*, 1922, **121**, 160, 1723, 1957, 2432.

[2] T. H. Fairbrother and A. Renshaw, *J.*, 1922, 134T.

There is evidence that the difficulties that have beset the manufacturer of dyestuffs in this country have not been peculiar to Great Britain. America, whose advance has followed very similar lines, has likewise suffered from the same cause. France claims to be in a position to supply 75% of her own requirements which are, however, small. The Swiss dye factories, whose interests are now pooled, continue to make headway and some distinctly novel ranges of products—principally in the realm of fast acid colours for wool—have been launched. In the main, however, they follow the German lead. There is no reason to believe that the German effort is being in any degree relaxed. Certain it is that she contemplates, with no little misgiving, the near approach of a time when the world's output of dyestuffs will greatly exceed the demand. Equally clear is it that she is shaping her course accordingly and developing those ramifications of the synthetic dyestuffs industry which have been regarded as side-lines, but which might conceivably become the main field of expansion, fostering the growth of seed, which may one day prove as fertile as that of the coal tar colour industry sown in this country by Perkin in 1856, and transplanted to bear a rich harvest of fruit in Germany.

SULPHONATION.

Investigation into the influence of temperature and the presence of the methyl group upon the speed of sulphonation of phenols has revealed the variability of the velocity with the temperature and the position of the methyl group. According to the conditions obtaining the influence may be one either of acceleration or retardation.[3]

Sodium, in the form of carbonate, has been recommended as catalyst in the further sulphonation of benzenemonosulphonic acid to benzenedisulphonic acid. Alternatively, vanadium pentoxide may be used with good catalytic effect.[4]

A simple method of separating the monosulphonic acids from the mixed sulphonic acids obtained by sulphonation of β-naphthylamine is described. This consists in dissolving the mixed acids in soda, and slowly adding to the solution the quantity of sulphuric acid theoretically required to precipitate the whole of the β-naphthylamine-8-sulphonic acid. The precipitate is practically pure β-naphthylamine-8-sulphonic acid. The β-naphthylamine-5-sulphonic acid remains in solution together with a small quantity of the 2.6 and 2.7 isomers.[5]

As an improvement upon the usual method for the commercial production of 1.4-naphtholsulphonic acid from α-nitronaphthalene, *via* naphthionic acid, it is proposed to start with α-naphthol, which is sulphonated at a comparatively low temperature in an inert solvent by means of chlorosulphonic acid.[6]

ALKALI FUSIONS.

A method of manufacturing dihydroxyanthraquinones consists in heating monochloroanthraquinones with aqueous caustic alkalis in presence of oxidising agents. Thus, Alizarin is obtained from 2-chloroanthraquinone by heating in an autoclave with caustic soda in presence of sodium chlorate.[7]

NITRO-COMPOUNDS.

Attention continues to be given to the mechanism of nitration of aromatic compounds, particularly phenol and toluene, upon which a vast amount of research was done during the war period. Evidence has been brought forward to show that in the nitration of phenol not only is the reaction facilitated by extensive presulphonation, but that the position of the sulphonic groups introduced has a marked influence. Thus a sulphonic group in the *p*-position to the hydroxy group is more readily displaced by a nitro group than is one in the *o*-position.[8] This supports the conclusions of previous workers.[9] The effect of conditions upon the products of nitration of toluene has been the subject of a detailed investigation.[10]

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[3] A. F. Campbell, *Chem. Soc. Trans.*, 1922, **121**, 847 ; *J.*, 1922, 496A.

[4] C. E. Senseman, *J. Ind. Eng. Chem.*, 1921, **13**, 1124 ; *J.*, 1922, 169A.

[5] G. R. Levi, *Giorn. Chim. Ind. Applic.*, 1921, **3**, 97 ; *J.*, 1921, 503A.

[6] Brit. Dyes. Corp., J. Baddiley, J. B. Payman and E. G. Bainbridge E.P. 186,515.

[7] A. H. Davies and Scottish Dyes, E.P. 174,101 ; *J.*, 1922, 212A.

By nitration of 5-nitroaceto-*m*-toluidine two new isomeric dinitrotoluidines have been prepared. When the nitration is performed in presence of sulphuric acid 5.6-dinitroaceto-*m*-toluidine forms the bulk of the product, whilst if fuming nitric acid alone is used the result is principally the 4.5 isomeride. The 5.6-dinitro-*m*-toluidine crystallises in orange-yellow plates, m.p. 165° C.; the 4.5-dinitro-*m*-toluidine forms large brownish-yellow needles, m.p. 141° C.[11] The nitration of tetrahydronaphthalene with mixed nitric and sulphuric acids, hitherto considered to be a practical impossibility, has been achieved. It is essential that the temperature during the reaction be kept below 50° C. Dinitro- and trinitrotetrahydronaphthalene can be obtained according to the conditions of working.[12]

The course of the reaction between *p*-nitrobenzenediazonium chloride and sodium sulphite has been elucidated, and ammonium sulphite established as an advantageous and inexpensive reducing agent for the production of *p*-nitrophenylhydrazine and its analogues.[13]

In studying the possibilities of nitrogen dioxide as a nitrating agent it has been found that, although unreactive towards aromatic hydrocarbons in the cold, at 80° C. it attacks benzene, converting it chiefly into 1.3.5-trinitrobenzene, oxalic acid, and substances of the aliphatic series. Phenol is readily nitrated when dissolved in a cold mixture of benzene and petroleum ether and treated with a solution of nitrogen dioxide in the same solvents, giving *o*- and *p*-nitrophenol free from tarry by-products. Acetanilide is not nitrated in the nucleus, but the acetyl group is removed and benzenediazonium nitrate formed.[14]

AROMATIC AMINES.

A good deal of work has been devoted to the catalytic reduction of nitrobenzene in vaporous form. It is claimed that a yield of 95% of aniline is obtained by passing nitrobenzene vapour mixed with hydrogen over a reduced nickel or copper catalyst at 192° C.[15] Reduction takes place at a lower temperature when cobalt is used in place of nickel. Iron carries the reduction further than copper, but cannot be used with the same freedom on account of its vigorous action. Silver is an excellent catalyst. A wide range of substances has been classified as catalytic or non-catalytic in this connexion.[16] The use of lead results in the formation of azoxybenzene, azobenzene, and aniline. Bismuth gives hydrazobenzene in addition. It appears that azobenzene is best obtained by employing lead catalyst prepared from yellow litharge.[17]

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[8] R. King, *Chem. Soc. Trans.*, 1921, **119**, 2105.

[9] M. Marqueyrol, P. Carré, and P. Loriette, *Bull. Soc. Chim.*, 1920, (IV.), **27**, 143.

[10] W. H. Gibson, R. Duckham, and R. Fairbairn, *Chem. Soc. Trans.*, 1922, **121**, 270.

[11] O. L. Brady, J. N. S. Day, and W. J. W. Rolt, *ibid.*, 1922, **121**, 526; *J.*, 1922, 363A.

[12] G. Schroeter and W. Schrauth, E.P. 148,923.

[13] W. Davies, *Chem. Soc. Trans.*, 1922, **121**, 715.

[14] H. Wieland, A. Bernheim, and P. Böhm, *Ber.*, 1921, **54**, 1776.

In the manufacture of aminoanthraquinones it has been found to be advantageous to start from chloroanthraquinones instead of, as hitherto, the corresponding sulphonic acids. Better yields of superior products are thereby obtained. Thus, an almost theoretical yield of 1-aminoanthraquinone is stated to be obtained by heating 1-chloroanthraquinone with aqueous ammonia in an autoclave. The presence of copper promotes the reaction.[18]

HALOGENATION.

A somewhat remarkable case of migration of a substituent halogen atom has been noticed in the production of β-chloro- or β-bromo-anthraquinone by heating the corresponding halogen-anthraquinone with concentrated sulphuric acid. Apparently the new position assumed by the halogen is always meta to that originally occupied, so that the conversion is only possible in those substances in which the meta-position is free.[19]

By direct chlorination, under suitable conditions, of 2-aminoanthraquinone suspended in nitrobenzene, chlorobenzene, or acetic acid it has been found possible to obtain a good yield of free 1-chloro-2-aminoanthraquinone, without previously protecting the amino group by acetylation.[20] Chlorination of toluene under different conditions shows that at an elevated temperature, in the absence of a catalyst, benzyl chloride is almost the sole product. The presence of lead chloride alters the course of the reaction, resulting in the formation of a mixture of the two isomeric chlorotoluenes containing about 62% of the ortho isomeride.[21] The employment of sodium carbonate, in quantity sufficient to neutralise the hydrochloric acid formed, is a feature of a process claimed for the manufacture of 1-chloro-4-hydroxyanthraquinone by passing chlorine through a nitrobenzene suspension of α-hydroxyanthraquinone.[22] The preparation of *p*-chlorobenzyl chloride by chlorination of benzyl chloride in presence of iodine as carrier is unsatisfactory, owing to the simultaneous formation of much of the ortho and traces of the meta-isomeride, as well as difficulty separable iodine derivatives.[23] Practically complete separation of the 2.5-dichloro- and 2.5.6-trichloro-toluene-4-sulphonic acids formed by chlorination, under suitable conditions, of toluene-*p*-sulphonic acid is possible by taking advantage of the great difference in the solubility in water of the respective sodium salts.[24] In the same way the separation of the products of chlorination of toluene-*o*-sulphonic acid—namely, the 4-chloro and 6-chloro derivatives, is effected.[25]

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[15] O. W. Brown and C. O. Henke, *J. Phys. Chem.*, 1922, **26**, 161; *J.*, 1922, 322A.

[16] O. W. Brown and C. O. Henke, *ibid.*, 1922, **26**, 272; *J.*, 1922, 406A.

[17] O. W. Brown and C. O. Henke, *ibid.*, 1922, **26**, 324; *J.*, 1922, 406A.

[18] J. Thomas, A. H. Davies, and Scottish Dyes, E.P. 173,006; *J.*, 1922, 170A.

[19] F. W. Atack and G. W. Clough, E.P. 169,732; *J.*, 1922, 840A.

[20] A. W. Fyfe and Brit. Dyes Corp., E.P. 173,166.

[21] A. Wahl, G. Normand, and G. Vermeylen, *Comptes rend.*, 1922, **174**, 946

Alizarin is more reactive than quinizarin towards bromine. According to the conditions of bromination the latter gives rise to quinizarinquinone or quinizarinquinone dibromide, whilst alizarin gives 3-bromoalizarin or 3-bromoalizarinquinone. In methyl alcoholic suspension, with ice cooling, quinizarin and alizarin are converted by bromine into quinizarinquinone methoxybromide and alizarinquinone methoxybromide respectively.[26]

Valuable contributions have been made to our knowledge of the application of sulphuryl chloride as a chlorinating agent. Heretofore, this substance has found little employment for the purpose, owing to the difficulty with which it reacts with benzenoid hydrocarbons under ordinary conditions. It has now been found that in the presence of suitable catalysts, *e.g.*, aluminium chloride together with some sulphur compounds, benzene can be readily chlorinated. Highly coloured intermediate compounds are formed during the reaction, which is almost exclusively one of chlorination.[27] When aniline is acted upon in the cold by sulphuryl chloride in ethereal solution a mixture of 2.4.6-trichloroaniline, 2.4-dichloroaniline, and *p*-chloroaniline is obtained, the two latter as hydrochlorides which are not further chlorinated in the cold. In boiling benzene the lower derivatives are completely chlorinated to 2.4.6-trichloroaniline. Anthranilic acid is similarly converted in ethereal solution into a mixture of 3.5-dichloro-2-aminobenzoic acid and 5-chloro-2-aminobenzoic acid (*m*-chloro), whilst in benzene solution it is chlorinated to 3.5-dichloro-2-aminobenzoic acid. *p*-Aminophenol reacts with sulphuryl chloride at 70° C, giving 2.3.5.6-

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[22] F. W. Atack and G. Robertson, E.P. 173,805.

[23] S. C. J. Olivier, *Rec. Trav. Chim.*, 1922, **41**, 419.

[24] Brit. Dyes Corp., A. G. Green, and D. A. Clibbens, E.P. 169,025.

[25] Brit. Dyes. Corp., A. G. Green, and A. E. Herbert, E.P. 170,056.

[26] O. Dimroth, E. Schutze, and F. Heinze, *Ber.*, 1921, **54**, 3035; *J.*, 1922, 51A.

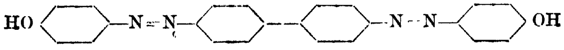
[27] O. Silberrad, *Chem. Soc. Trans.*, 1921, **119**, 2029; *J.*, 1922, 93A.

tetrachloro-4-dichloroamino-1-hydroxybenzene, m.p. 71·5° C.[28] The products of the reaction between pyrosulphuryl chloride and toluene in presence of aluminium chloride under different conditions have been the subject of investigation.[29]

OXIDATION.

The trend of investigation has been chiefly in the direction of oxidation by electrolytic methods and development of processes for air oxidation of hydrocarbons through the medium of a catalyst.

It appears that electrolytic oxidation of leuco-Malachite Green only takes place in the presence of a catalyst, the most suitable for the purpose being uranyl sulphate. High temperature and low concentration favour the reaction.[30] The product of electrolytic oxidation of azobenzene described by Heilpern as tetrahydroxyazobenzene appears, on further investigation, to be a complex mixture from which *pp*-dihydroxyazobenzene and *bis*-phenyl-*pp*-disazophenol



have been isolated.[31]

Anthraquinone has been prepared by passing a mixture of anthracene vapour and air over powdered pumice coated with vanadic acid.[32] The use of titanium compounds as oxygen carriers has also been recommended.[33] The presence of a small quantity of oxide of nitrogen acts similarly when anthracene and its derivatives, in solution or suspension, are subjected to the action of oxygen under pressure.[34] In employing the latter process excellent yields of high quality are claimed in the presence of an agent which readily fixes nitric acid, such as sodium acetate, whereby the reaction may be carried out in an acid solvent or suspension which need not necessarily be anhydrous.[35] Phthalic anhydride is made by air oxidation of naphthalene in presence of vanadyl chloride,[36] vanadium pentoxide, molybdenum trioxide,[37] or titanium compounds.[38]

The important discovery has been reported that in presence of a suitable oxygen carrier such as oxide of vanadium or molybdenum,

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[28] W. Eller and L. Klemm, *Ber.*, 1922, **55**, 217.

[29] W. Steinkopf and K. Buchheim, *Ber.*, 1921, **54**, 2963.

[30] A. Lowry and E. H. Haux, *Trans. Amer. Electrochem. Soc.*, 1921, 99.

[31] F. Fichter and W. Jaeck, *Helv. Chim. Acta*, 1921, **4**, 1000.

[32] A. Wohl, E.P. 156,244 ; *J.*, 1922, 407A.

[33] F. W. Atack, E.P. 182,843 ; *J.*, 1922, 662A.

[34] Chem. Fabr. Worms, A.G., E.P. 156,215, 156,538, 156,540 ; *J.*, 1922, 407A.

[35] Chem. Fabr. Worms, A.G., E.P. 169,145 ; *J.*, 1922, 496A.

[36] Brit. Dyes. Corp., A. G. Green, and J. W. Porter, E.P. 164,785.

[37] C. Conover and H. D. Gibbs, *J. Ind. Eng. Chem.*, 1922, **14**, 120.

[38] F. W. Atack, E.P. 182,843 ; *J.*, 1922, 662A.

α-nitronaphthalene is converted by oxidising agents into phthalimide without any formation of nitrophthalic acid.[39] Under conditions hitherto employed only nitrophthalic acid has resulted, owing to the resistance to oxidation offered by the ring containing the nitro group.

In view of doubts expressed as to the nature of the blue oxidation product of diphenylamine, it is to be noted that confirmatory evidence has been brought forward that this compound is an imonium salt of NN-diphenylbenzidine.[40]

CONDENSATION.

Whereas the normal product of the reaction between phthalic anhydride and phenol in sulphuric acid is phenolphthalein, in presence of boric acid the reaction takes an entirely different course, resulting in the formation of α-hydroxyanthraquinone. Similarly, phenol-*p*-sulphonic acid gives 1-hydroxyanthraquinone-4-sulphonic acid, which on further treatment with sulphuric acid is converted into quinizarin. By adopting suitable conditions the same end product can be obtained direct from phenol.[41] Another striking example of the influence of boric acid is seen in the condensation of phthalic anhydride with resorcinol. Under ordinary conditions the preparation of Fluorescein is attended by the formation of only traces of resorcinolphthalein. In presence of boric acid, however, fair yields of the latter are obtained.[42]

In the condensation of *o*-benzoylbenzoic acid to anthraquinone it is claimed that diluted sulphuric acid is as efficient as concentrated acid.[43] The product formed by dehydration of the *o* dimethylbenzoylbenzoic acid, obtained by interaction of *o*-xylene and phthalic anhydride in presence of aluminium chloride, which has hitherto been regarded as 2.3-dimethylanthraquinone, has now been identified as a mixture of the two isomerides 1.2-dimethylanthraquinone and 2.3-dimethylanthraquinone.[44] Tetrahydronaphthalene and phthalic anhydride condense, in presence of aluminium chloride, with benzene as dilutent, to β-tetrahydronaphthoyl-*o*-benzoic acid which, under the influence of fuming sulphuric acid, yields a mixture of α- and β-tetrahydronaphthanthraquinone.[45] Internal condensation products are formed by the action of fuming sulphuric acid upon 1-nitro-2-alkyl-anthraquinones, by the elimination of a molecule of water. These are probably iso-oxazole derivatives of the type

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[39] Brit. Dyes. Corp., A. G. Green and S. J. Green, E.P. 183,044; *J.*, 1922, 663A.

[40] F. Kehrmann and G. Roy, *Ber.*, 1922, **55**, 156.

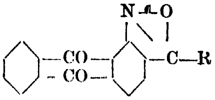
[41] D. Segaller, D. H. Peacock, and Brit. Dyes. Corp., E.P. 176,925; *J.*, 1922, 408A.

[42] O. Fischer and M. Bollman, *J. prakt. Chem.*, 1922 (ii), **104**, 123.

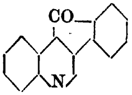
[43] F. W. Atack, E.P. 176,235; *J.*, 1922, 323A.

[44] A. Fairbourne, *Chem. Soc. Trans.*, 1921, **119**, 1573.

[45] Tetralin Ges.. G.P. 346,673; *J.*, 1922, 497A.



and are described as extremely reactive compounds which constitute valuable intermediates for the manufacture of anthraquinone dyestuffs.[46] New ketonic substance of the quinoline series, described as useful dyestuff intermediates, are prepared by heating 3-phenylquinoline-4-carboxylic acids with concentrated sulphuric acid.[47] They are of the type



Interest continues in the reaction between carbonyl chloride and benzene in presence of aluminium chloride. Attempts to produce anthraquinone in this way, however, have not yet succeeded.[48]

HYDROGENATED NAPHTHALENE DERIVATIVES.

Tetrahydronaphthalene compounds have been widely investigated, and much work on the nitro-, amino-,[49] sulpho-, and hydroxy-derivatives[50] has been reported. ar-Tetrahydro-β-naphthol is prepared by sulphonating tetrahydronaphthalene and subjecting the alkali salt of the resulting sulphonic acid to alkali fusion. The yield by this method is better than that obtained by hydrogenation of β-naphthol.[51] A study of the formation of ar-tetrahydro-α-naphthol by reduction of α-naphthol with alcoholic sodium, has shown that the course of the reaction is the same as that in the hydrogenation of α-naphthylamine and of naphthalene under the same conditions.[52]

In opposition to previous contentions it is now claimed that tetrahydronaphthalene can be readily nitrated by mixed nitric and sulphuric acids, provided the temperature and the amount of water present be controlled within certain defined limits.[53]

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[46] Meister, Lucius, und Brüning, E.P. 147,001, 160,433 ; *J.*, 1922, 50A.

[47] Meister, Lucius, und Brüning, G.P. 343,322 ; *J.*, 1922, 135A.

[48] R. E. Wilson and E. W. Fuller, *J. Ind. Eng. Chem.*, 1922, **14**, 406.

[49] *Annalen*, 1922, **426**, 17 ; *J.*, 1922, 133A.

[50] *Ibid.*, 1922, **426**, 83 : *J.*, 1922, 133A.

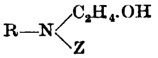
[51] G. Schroeter and W. Schrauth, E.P. 148,408.

[52] F. M. Rowe and E. Levin, *Chem. Soc. Trans.*, 1921, **119**, 2021 ; *J.*, 1922, 93A.

[53] G. Schroeter and W. Schrauth, E.P. 148,923.

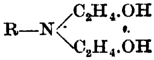
SULPHATO (ALCOHOLIC SULPHONIC ACID) COMPOUNDS.

An entirely new principle, apparently susceptible of very wide application in dyestuff manufacture, is presented in the introduction of an acidic group (SO_4H), for which the name of "sulphato" has been proposed.[54] This group is introduced into primary or secondary aromatic amino compounds, its presence conferring properties similar to those associated with the sulphonic group, that is to say solubility in aqueous solutions and ability to dye animal fibres from an acid dyebath. In general the sulphato group is introduced in two stages, the first of which consists of a conversion of the amine by the action of ethylenechlorhydrin, or a homologue, into a hydroxyalkylamine of the type



$$R{-}N\begin{matrix}\diagup C_2H_4.OH\\ \diagdown Z\end{matrix}$$

or



$$R{-}N\begin{matrix}\diagup C_2H_4.OH\\ \diagdown C_2H_4.OH\end{matrix}$$

where R represents a substituted or non-substituted aromatic residue, and Z is hydrogen, alkyl, aryl, etc. Thus, aniline gives either mono- (I.) or di- (II.) oxyethyl-aniline.

$C_6H_5NH.C_2H_4OH$ I. $C_6H_5N(C_2H_4OH)_2$ II.

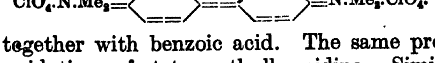
The second stage is effected by simple treatment with concentrated sulphuric acid, whereby the sulphato-compound is formed, *e.g.*, disulphato-diethylaniline, $C_6H_5.N(C_2H_4.SO_4H)_2$. Alternatively, the conversion of the amine into a sulphato-alkylamine may be effected in one step by reacting upon it in a neutral or alkaline solution with chloroethyl hydrogen sulphate ($C_2H_4.Cl.SO_4H$), prepared by dissolving ethylenechlorhydrin in concentrated sulphuric acid:

$$C_6H_5NH_2+2C_2H_4ClSO_4H \rightarrow C_6H_5N(C_2H_4.SO_4H)_2+2HCl.$$

The sulphato-alkylarylamines react analogously to the alkylarylamines, and like the latter, can be coupled with diazo-compounds, condensed with aldehydes, etc. The development of this new phase in the technical applications of colour chemistry will be watched with interest.

TRIARYLMETHANE DYES.

It is known that over-oxidation of leuco-triphenylmethane dyes occurs if excess of lead peroxide be used. In the case of leuco-Malachite Green tetramethyldiphenoquinone-imonium perchlorate,



is formed, together with benzoic acid. The same product results from the oxidation of tetramethylbenzidine. Similarly, leuco-

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[54] A. G. Green, K. H. Saunders, and Brit. Dyes Corp., E.P. 181,750; *J.*, 1922, 625A.

Brilliant Green and tetra-ethylbenzidine yield tetra-ethyldiphenoquinone-imonium perchlorate.[55]

New red mordant dyes are prepared by condensing a methylenedisulphodiarylido-*o*-hydroxycarboxylic acid, formed from two molecules of an arylido-*o*-hydroxycarboxylic acid, containing a sulphonic acid group in the aryl nucleus, with formaldehyde. On chromed wool or cotton the dyes give fast bright-red shades. It is claimed that for printing, especially, they possess advantage over the corresponding non-sulphonated dyes, both in brightness and in fastness.[56]

Recent work on the furane analogue of Malachite Green has apparently established the fact that, in addition to the reduced product, diaminodiphenylfurylmethane, possessing a light yellow colour, the dyestuff, both in the form of zinc chloride double salt, and as oxalate, is more deeply coloured than Malachite Green. Dyeings made from the two dyes are indistinguishable as regards fastness to light, alkali, milling, etc. That of the furane compound is grey-blue.[57]

It is claimed that direct affinity for unmordanted cotton is possessed by basic triarylmethane dyes obtained by condensing arylbenzthiazoles, such as dehydrothiotoluidine, with Michler's hydrol, followed by oxidation. The new dyes dye unmordanted cotton very bright shades of green, whilst the shades on wool and tannin-mordanted cotton are said to be faster than those of known green basic dyes.[58]

Superior solubility in dyes of the triarylmethane series is effected by introducing oxyalkyl groups attached to nitrogen. Thus, the dyestuff corresponding with Victoria Blue R, but containing a hydroxyethyl group in place of an ethyl group, has similar properties, but is distinguished by greater solubility.[59]

Azo Dyes.

Again azo dyes have occupied first place in point of volume of research carried out in dyestuff chemistry. This is, undoubtedly, due to the vast possibilities of the azo reaction, in the realm of which new fields are constantly being opened out, and to the comparatively ready attainment, within the series, of products possessing beauty and brilliancy of shade coupled with a degree of fastness formerly only associated with the more costly dyes of other categories. Moreover, the advent of certain groups of azo-colours has been hailed by the dyer not only because of these fine qualities, but also because they mark a new era in the practice of dyeing, by virtue of greater ease of application, shortening of process, and consequent beneficial effect upon the material dyed.

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[55] F. Kehrmann, G. Roy, and M. Ramm, *Helv. Chim. Acta*, 1922, **5**, 153; *J.*, 1922, 287A.

[56] Durand and Huguenin, U.S.P. 1,403,888; *J.*, 1922, 170A.

[57] R. R. Renshaw and N. M. Naylor, *J. Amer. Chem. Soc.*, 1922, **44**, 862; *J.*, 1922, 365A.

[58] Brit. Dyes. Corp., J. Baddiley, E. H. Rodd, and H. L. Stocks, E.P. 186,517; *J.*, 1922, 934A.

[59] Brit. Dyes. Corp., A. G. Green, K. H. Saunders, and S. C. Bate, E.P. 185,612; *J.*, 1922, 852A.

There has been continued activity in investigating soluble metallic lakes, principally those of chromium and copper, of azo dyes, aiming at the production in a single stage of dyed shades comparable in fastness to light and washing with those formerly achieved only through the medium of separate treatment with metallic salts. Direct cotton dyes, fast to light and ironing, are prepared by treating azo dyestuffs, from 5.5′-dihydroxy-2.2′-dinaphthylamine-7.7′-disulphonic acid and a diazotised amine containing a sulphonic or carboxylic acid group in ortho position to the amino group, with copper compounds.[60] Soluble red-violet to blue-violet lakes are obtained when azo dyestuffs prepared by coupling diazotised anthranilic acid, or its derivatives, with β-naphthylamine, or its sulphonic acids, are boiled with chromium fluoride.[61]

The combination of diazotised 1-amino-2-hydroxynaphthalene-4-sulphonic acid with halogen substitution products of α-naphthol has been found to result in dyes which dye wool from an acid bath red-violet shades changing to grey to blue on chroming. If, however, these dyestuffs are boiled in aqueous solution with chromium salts they yield soluble chromium dyes possessing good levelling properties and capable of giving shades fast to light upon wool from an acid bath. Thus, the chromium compound from 1-amino-2-hydroxynaphthalene-4-sulphonic acid and 1-hydroxy-5.8-dichloronaphthalene dyes a fast greenish-blue shade.[62]

A new series of mordant azo dyes which can be applied to wool by either the "on-chrome," "after-chrome," or "metachrome" process, is available in products obtained by coupling polyhalogen-2-diazo-hydroxy-derivatives of the benzene series with acidylamino-hydroxynaphthalenesulphonic acids. For example, 3.4.5-trichloro-2-amino-1-hydroxybenzene gives with 1-acetylamino-8-hydroxy-naphthalene-4-sulphonic acid a dyestuff which dyes wool with chrome mordant a blue shade fast to light, washing, and milling.[63] Related in type are the monoazo dyes derived from picramic acid and a 2-acidylaminophenol containing a monovalent substituent group in position 4. Thus, the dyestuff

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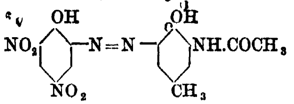
[60] F. Bayer und Co., E.P. 165,083 ; *J.*, 1922, 664A.

[61] F. Bayer und Co., E.P. 170,155 ; *J.*, 1922, 841A.

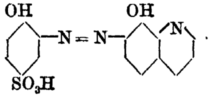
[62] Soc. Chem. Ind. Basle, U.S.P. 1,402,350 ; *J.*, 1922, 137A.

[63] W. Herzberg and O. Scharfenberg. U.S.P. 1,408,297 ; *J.*, 1922, 288A.



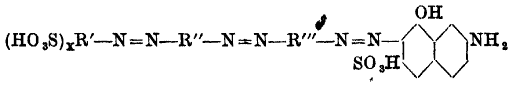
gives olive-brown shades on wool, of excellent fastness to light, washing, milling, and potting.[64]

An interesting coupling component for the production of fast chroming dyes has been found in hydroxyquinoline. When 2-amino-1-hydroxybenzene-4-sulphonic acid is used as the diazotisable amine along with 8-hydroxyquinoline, the resulting dyestuff



dyes wool from an acid bath a brown shade, which, on after-treatment with bichromate, changes to a bordeaux, fast to light and milling.[65]

New level-dyeing trisazo direct dyes of the type



dye cotton reddish-blue shades which, when developed on the fibre with β-naphthol or *m*-diamines, are converted into bluish greys fast to light and washing (R′ represents an aromatic radicle, R″ and R‴ being sulphonated or unsulphonated aromatic radicles).[66]

In the insoluble azo colour series produced *in situ* on the fibre a distinct step forward has been made in the introduction of stable mixtures of a nitrosamine salt of a diazo compound and a hydroxynaphthalene compound. A range of such mixtures is now in commercial use.[67] They consist in general of the stable diazo salts of bases mixed with naphthols, naphtholcarboxylic acids, naphtholcarboxylic acid arylides, etc., and present a simplified method of producing the respective shades. Their application is, indeed, simple, the colours being developed by merely steaming. This promises to be an important advance from a calico-printing point of view. Some representative members of this group are Rapid Fast Red GL,[68] Rapid Fast Red 3GL, Rapid Fast Red GG,

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[64] W. Lange, U.S.P. 1,408,363 ; *J.*, 1922, 288A.

[65] R. Haugwitz, U.S.P. 1,419,500 ; *J.*, 1922, 583A.

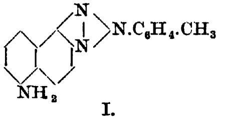
[66] J. Dedichen, U.S.P. 1,416,621 ; *J.*, 1922, 497A.

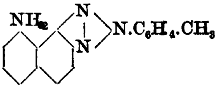
[67] Products of the Farbfab. Griesheim-Elektron.

[68] F. M. Rowe and E. Levin. *J. Soc. Dyers and Col.*, 1921, 37, 204.

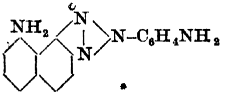
Rapid Fast Red B, which consist of the anilide of β-hydroxynaphthoic acid mixed with *o*-nitro-*p*-toluidine, *p*-chloro-*o*-nitroaniline, *p*-nitroaniline, and 5-nitro-*o*-anisidine respectively; and Rapid Fast Red BB which is a mixture of the *p*-nitroanilide of β-hydroxynaphthoic acid with the nitrosamine salt of 5-nitro-*o*-anisidine.[69]

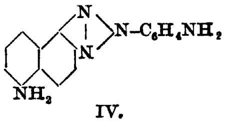
Much attention has been given to the preparation of new intermediates for azo dyestuff manufacture. The newly-described "sulphato" compounds, which comprise intermediates for a wide range of dyestuff categories, are dealt with on page **93.** Promising results have been obtained in the aminonaphthotriazole series. For example, 5-amino-1.2-naphtho-*p*-tolyltriazole (I.), obtained by oxidation of *p*-toluene-1-azo-5-nitro-β-naphthylamine and reduction of the nitro group, is useful as a first, but not as a middle, component of polyazo dyes. (The amino group in position 5 is somewhat unreactive.)[70] On the other hand the isomeric 8-amino-1.2-naphtho-*p*-tolyltriazole (II.),


I.


II.

prepared in a similar manner from the corresponding 8-amino compound, is found to be much more reactive, indicating its possible utility as a middle component for polyazo dyes. Both 8-amino-1.2-naphtho-4-aminophenyltriazole (III.), and 5-amino-1.2-naphtho-4-aminophenyltriazole (IV.),


III.


IV.

obtained by reduction of the corresponding nitro compounds, are readily diazotised in aqueous solution, and the resulting bisdiazonium salts couple easily with naphtholsulphonic acids to form disazo dyes.[71]

The availability of methylamine hydrochloride on a commercial scale has facilitated the production of alkyl compounds of the type: 2-aryl-*p*-sulphonyl-2-alkyl-1.2-naphthylenediamine and their sulphonic acids, which investigation has shown to possess valuable properties as intermediates: 2-toluene-*p*-sulphonyl-2-methyl-1.2-

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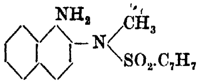
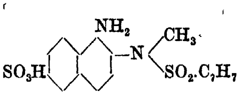
[69] Private communication from F. R. Stafford.

[70] G. T. Morgan and S. Chazan, *J.*, 1922, 1T.

[71] G. T. Morgan and H. Gilmour, *J.*, 1922, 61T.

naphthylenediamine and 2-toluene-*p*-sulphonyl-2-methyl-1.2-naphthylenediamine-6-sulphonic acid



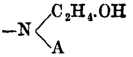


prepared by the action of toluene-*p*-sulphonic chloride or methyl-β-naphthylamine and methyl-β-naphthylamine-6-sulphonic acid respectively, followed by nitration and reduction, can be employed as primary, middle, and end components in the formation of complex azo colours. When they are used as coupling components the resulting dyes are characterised by their greater brilliancy as compared with the corresponding dyes from α-naphthylamine or Cleve's acid. This striking difference is attributed to the presence of the substituted side chain -$N(CH_3)\cdot SO_2\cdot C_7H_7$ in the β-position. Whereas the unsulphonated diamine presents a serious technical difficulty in that its sparing solubility renders diazotisation in aqueous media slow, the sulphonic acid is free from this disadvantage.[72]

Azo colours having the properties of sulphide dyes are described. When chlorodinitrobenzene is condensed with dehydrothiotoluidine, and the product reduced with ammonium sulphide, a base is formed which, when diazotised and coupled with α- or β-naphthylamine, gives a product which dyes cotton bluish-red from a sulphide bath.[73]

AZINE, OXAZINE, AND THIAZINE DYES.

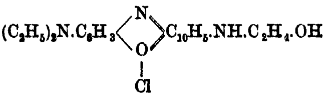
It has been claimed that by the application of standard reactions for the preparation of dyestuffs of this group to intermediates containing one or more hydroxyalkyl groups attached to nitrogen,



$$-N\begin{cases}C_2H_4.OH\\A\end{cases}$$

A = oxyalkyl, alkyl, hydrogen, etc.

dyestuffs are obtained which possess important advantages, in properties and ease of manufacture, over those derived from the corresponding ordinary alkyl compounds. They may have basic properties, or sulphonic acid or mordant-dyeing groups. The following typical examples may be cited :—



$$(C_2H_5)_2N.C_6H_3\langle{}^{N}_{O}\rangle C_{10}H_5.NH.C_2H_4.OH \quad (O-Cl)$$

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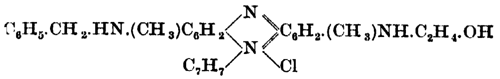
[72] G. T. Morgan and H. Gilmour, *J.*, 1922, 3T.

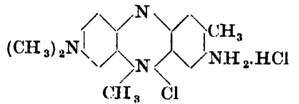
[73] E. Koechlin, *Bull. Soc. Ind. Mulhouse*, 1921, 341.

prepared from nitroso-diethyl-*m*-aminophenol hydrochloride and hydroxyethyl-*a*-naphthylamine hydrochloride, which dyes tannin-mordanted cotton almost the same shade as Nile Blue 2B, but has considerably greater solubility.

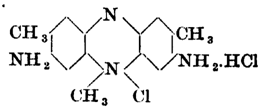


from 4-*p*-tolyl-2-benzyl-toluylene-*m*-diamine and nitroso-hydroxy-ethyl-*o*-toluidine hydrochloride. The shade is the same as that of Brilliant Rhoduline Red; the solubility is better. In general, the main effect of the introduction of the oxyalkyl group appears to be increased solubility.[74]

As the result of an elaborate investigation, it has transpired that the constitution (I.) hitherto assigned to the dyestuff known commercially as Azine Scarlet is incorrect, and that actually (II.) represents the constitution of this colour.



I.



II.

The accumulation of alkyl groups in the molecule increases the blueness of the shade, the dyestuff corresponding to formula (I.) being a magenta-coloured substance.[75]

Azine condensation products of phenanthraquinone with 1.2-naphthylenediamine and 1.2-naphthylenediamine-5-sulphonic acid have been prepared containing amino- and hydroxy-auxochromic groups. These phenanthranaphthazines dye wool from an acid bath in bright yellow to dark brown shades. By introducing one or more anilido groups into the phenanthraquinone molecule green to violet shades are obtained.[76] A number of insoluble substituted naphthaflavindulines which, in a finely-divided state, dye bright red to blue shades on wool from an acid bath, are described.[77] Whether these dyes possess the necessary properties of fastness to render them technically useful, or whether they are merely of scientific interest, is not yet disclosed.

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[74] Brit. Dyes. Corp., A. G. Green, K. H. Saunders, and E. B. Adams E.P. 132,031; J., 1922, 626A.

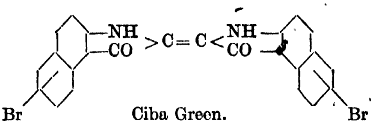
[75] J. B. Cohen and H. G. Crabtree, *Chem. Soc. Trans.*, 1921, **119**, 2055 J., 1922, 94A.

[76] A. C. Sircar and S. Dutt, *ibid.*, 1922, **121**, 1944; J., 1922, 852A.

[77] S. Dutt, *ibid.*, 1922, 122, 1952; J., 1922, 852A.

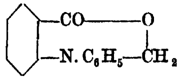
VAT DYES.

There is comparatively little to record in the way of distinctly new lines of research or manufacture. The synthesis of 2.3.2′.3′-naphthindigo by a parallel method to that of indigo from anthranilic acid appears to give but poor yields. β-Hydroxynaphthoic acid is the starting point, and is first converted by heating in a current of ammonia under the influence of ammonium chloride and ammoniacal zinc chloride, into 2.3-aminonaphthoic acid. This is condensed with chloroacetic acid and gives a quantitative yield of 2.3-naphthylglycinecarboxylic acid, from which, however, only a poor yield of 2.3.2′.3′-naphthindigo is obtainable by the usual methods. The latter dyes greenish-blue shades. Bromination changes the shade to a green fast to light, but not fast to chlorine. Brominated 2.3.2′.3′-naphthindigo is probably closely allied to the dibromo-bis-β-naphthindigo known commercially as Ciba Green G (S.C.I.), in which, instead of being attached to the 2.3-positions, the imino and carbonyl groups are attached to the 1.2-positions in the naphthalene rings.[78]

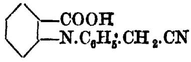


Ciba Green.

Attempts to prepare peri-naphthindigo from 1.8-naphthylglycinecarboxylic acid have proved unsuccessful, failure being attributed to the unstable character of the naphthylglycine.[79] N.N′-Diphenylindigotin has been synthesised from N-phenylanthranilic acid. By the action of formaldehyde on the latter the formalide



is obtained which, on treatment with potassium cyanide furnishes the nitrile



On hydrolysis this gives N-diphenylglycine-o-carboxylic acid, from which phenylindoxyl is prepared by the action of sodium acetate and acetic anhydride, or of caustic soda. Oxidation of phenylindoxyl in faintly alkaline solution with potassium ferricyanide results in N.N′-diphenylindigotin

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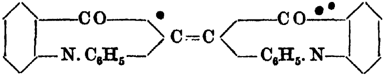
[78] H. E. Fierz and R. Tobler, *Helv. Chim. Acta*, 1922, **5**, 557; *J.*, 1922, 625A.

[79] H. E. Fierz and R. Sallmann, *ibid.*, 1922, **5**, 560; *J.*, 1922, 625A.

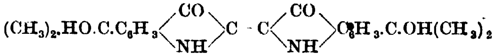


Owing to the instability of the molecule due to the presence of N-phenyl groups, the dyestuff is of no practical value.[80]

A new dye resembling indigo in appearance, and dyeing greenish-blue shades on cotton from a hydrosulphite vat, has been prepared from mononitrocymene. The latter is oxidised to *o*-nitro-*p*-*a*-hydroxyisopropylbenzoic acid which, on reduction with ferrous sulphate and barium hydroxide, gives the corresponding amino compound. This is condensed with chloroacetic acid to *o*-aminoacetic-*p*-*a*-hydroxyisopropylbenzoic acid,

$$C(CH_3)_2(OH).C_6H_3.(COOH).NH.CH_2.COOH,$$

which is converted by potash fusion and oxidation into the dyestuff,[81]



$$(CH_3)_2.HO.C.C_6H_3\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C-C\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_3.C.OH(CH_3)_2$$

When an alcoholic suspension of indigo is boiled with hydrazine and caustic soda, desoxindigo, *i.e.*, indigo in which one of the CO groups is replaced by a CH_2 group, is formed which has no value as a vat dye. The sodium salt of its monosulphonic acid dyes wool a golden yellow shade, which is fugitive to light. Similar desoxy compounds are obtainable in like manner from 5.5′-dimethylindigotin, 7.7′-dimethylindigotin, and dibromoindigotin. On the other hand, Thioindigo Red, when thus treated, is merely reduced to its leuco compound.[82]

It is reported that good yields of indigo have been obtained by alkali fusion of dianilidosuccinic acid, followed by air oxidation.[83]

The reaction whereby a blue coloration results from warming a solution of 1.8-nitronaphthalenesulphinic acid with zinc dust and potassium sulphite[84] is an interesting one involving the formation of a new vat dyestuff containing sulphur, to which the name of Naphthothiam Blue has been given. 1.8-Nitronaphthalenesulphinic acid is first reduced in cold caustic soda solution with ferrous sulphate to 1.8-naphthylaminesulphinic acid, which, on warming in slightly acid aqueous solution, gives, in addition to a small quantity of a bluish-green substance, an anhydro derivative of aminonaphthalenesulphinic acid (I.) (naphthothiam). This is soluble in caustic soda, but insoluble in sodium carbonate. Boiling with dilute mineral acid converts naphthothiam quantitatively into Naphthothiam Blue (II.)

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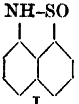
[80] P. Friedländer and K. King, *Ber.*, 1922, **55**, 1597 ; *J.*, 1922, 582A.

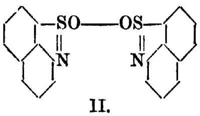
[81] M. Phillips, *J. Amer. Chem. Soc.*, 1922, **44**, 1775 ; *J.*, 1922, 743A.

[82] W. Borsche and R. Meyer, *Ber.*, 1921, **54**, 2854 ; *J.*, 1921, 881A.

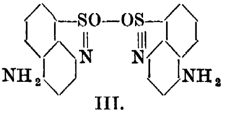
[83] G. C. Bailey and R. S. Potter, *J. Amer. Chem. Soc.*, 1922, **44**, 215 ; *J.*, 1922, 246A.

[84] Erdmann and Süvern, *Annalen*, 1893, **275**, 230.


I.

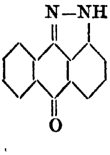

II.

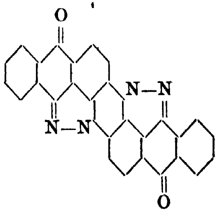
In appearance the new dye closely resembles indigo, dissolving in an alkaline hydrosulphite vat with a brownish-yellow colour. Wool, and to a less extent cotton, is dyed a dull blue shade. A similar blue vat colour (III.) containing two amino groups may be prepared in an analogous manner from 1-nitro-acetyl-4-amino-naphthalene-8-sulphinic acid.[85]


III.

It is claimed that by chlorination or bromination of the commercially unimportant 5.5′-dimethylindigo the dull shade of the latter is transformed into a bright colour of increased fastness.[86] New yellow to orange vat dyes fast to chlorine and soap are obtained by condensing an oxazine compound with a quinonoid compound containing a halogen in the quinonoid nucleus, as, for example, 2-chloro- or 2.3-dichloro-1.4-naphthoquinone, etc.[87]

The dyestuff obtained by oxidation of dibenzanthrone is rendered fast to acids and chlorine by introduction of methyl groups. At the same time the colour is changed from olive-green to greenish-blue.[88] It now appears that Pyrazolanthrone Yellow obtained by alkali fusion of pyrazolanthrone (I.)[89] does not conform in its behaviour to the constitution (II.) orginally assigned to it.


I:


II.

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[85] A. Reissert, *Ber.*, 1922, **55**, 858 ; *J.*, 1922, 364A.

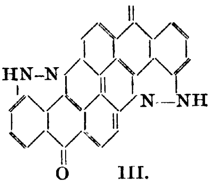
[86] Soc. Chim. des Usines du Rhône, E.P. 152,634 ; *J.*, 1922, 841A.

[87] Akt.-Ges. für Anilin-Fabr., U.S.P. 1,419,502 ; *J.*, 1922, 583A.

[88] A. H. Davies, R. F. Thomson, J. Thomas, and Scottish Dyes, E.P. 181,304.

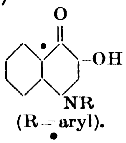
[89] Chem. Fab. Griesheim-Elektron, G.P. 255,641.

A study of its chemical reactivity, *e.g.*, ability to form a potassium salt, dibenzyl, dibenzoyl compounds, etc., has established the presence of replaceable hydrogen atoms and led to the conclusion that this colouring matter is correctly represented by the structural formula (III.). This is supported by the fact that substituted derivatives of Pyrazolanthrone Yellow are obtained from substituted pyrazolanthrones in which the position 1 or 4 is occupied, whilst with a substituent in position 8 either no condensation takes place, or the substituent is expelled.[90]

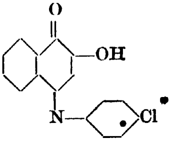


III.

A green vat dye suitable for pigments is said to result from heating α-naphthoquinone with water at 150°C.[91] Green to black sulphurised vat dyes are prepared by treating with a suitable sulphurising agent β-hydroxynaphthoquinone-anilido compounds of type (I.)



I.

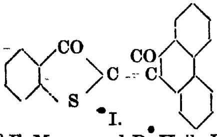


II.

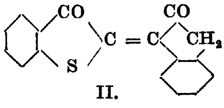
such, for example, as (II.) obtained by condensing *p*-chloro-aniline with 1.2-naphthoquinone-4-sulphonic acid.

The shades dyed upon wool from a hydrosulphite vat are said to be capable of development with chromium salts in an acid bath. Those dyes of the series which contain a sulphonic or carboxylic acid group are credited with acid-mordant dyeing properties.[92]

A number of new indigoid vat dyes of the phenanthrene and indene series have been prepared; *e.g.*, 2-thionaphthene-9′-phenanthrene-indigo (I.)



I.



II.

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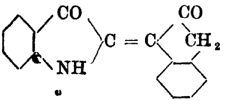
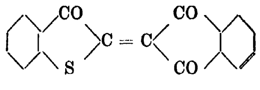
[90] F. Mayer and R. Heil, *Ber.*, 1922, **55**, 2155; *J.*, 1922, 663A.

[91] Bad. Anilin und Soda Fabrik, E.P. 168,447.

[92] Cassella, E.P. 151,000; *J.*, 1922, 136A.

obtained by condensation of phenanthrenequinone with 3-oxythionaphthene, gives dull violet shades from a yellow vat. Contrasted with the similarly constituted thionaphthene-acenaphthene-indigo (Thioindigo Scarlet 2G) the new dyestuff is extraordinarily resistant towards caustic alkalis. 2-Thionaphthene-1′-indone-indigo (II.), from β-ketohydrindene and thionaphthenequinone-2-anilide, dyes bordeaux shades redder than those of the corresponding indole-dyestuff, 2-indole-1′-indone-indigo (III.)

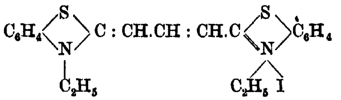

III.


IV.

which is the condensation product of β-ketohydrindene with α-isatinanilide. Thionaphthenequinone-2-anilide condensed with αγ-indanedione gives rise to the dyestuff 2-thionaphthene-2′-indoneindigo (IV.), which on alkaline reduction goes through a brownish-violet stage to a brown-coloured vat.[93]

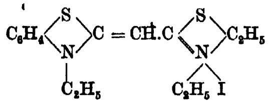
CYANINE DYES.

The formation of the isocyanines by the action of alkalis on a mixture of a quinoline and a quinaldine alkyl iodide has its parallel in the benzthiazole series.[94] Recent investigation has shown that when benzthiazole ethiodide and 1-methylbenzthiazole ethiodide are heated together in pyridine solution, for several hours on a water bath, a deep purple-red colour is developed. On standing, a crystalline deposit separates out which is a mixture of a purple dye belonging to the carbocyanine class and probably possessing the constitution,



$$C_6H_4\left\langle{}^{S}_{\underset{C_2H_5}{N}}\right\rangle C:CH.CH:CH.C\left\langle{}^{S}_{\underset{C_2H_5\ I}{N}}\right\rangle C_6H_4$$

and a yellow dyestuff analogous to the cyanines and proved to have the constitution



$$C_6H_4\left\langle{}^{S}_{\underset{C_2H_5}{N}}\right\rangle C=CH.C\left\langle{}^{S}_{\underset{C_2H_5\ I}{N}}\right\rangle C_2H_5$$

to which the name Thiocyanine is given.

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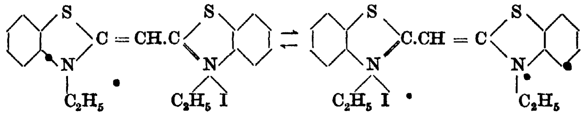
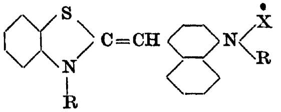
[93] P. Friedländer, W. Herzog, and G. von Voss, *Ber.*, 1922, **55**, 1591; *J.*, 1922, 582A.

[94] Hofmann, *Ber.*, 1887, **20**, 2262.

Both dyestuffs are powerful photographic sensitisers.[95] The results of a recent investigation point to the probability of a type of virtual tautomerism existing in the dyes of the class, represented thus :—[96]



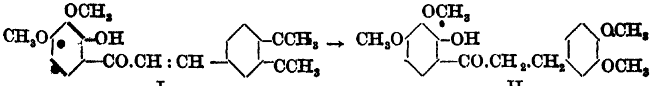
A further development in the range of photosensitising cyanine dyes is seen in the production of a series intermediate between the thiocyanines and the isocyanines. The members of this series contain one quinoline and one benzthiazole nucleus, and are prepared by the action of sodium hydroxide in alcoholic solution upon a mixture of a quinoline alkyliodide and a 1-methylbenzthiazole alkyliodide. They are, therefore, closely related in method of formation as well as in properties to the isocyanines, and are probably represented by the formula



The name thioisocyanines is proposed for these mixed compounds. It is interesting to note that, owing to the instability of the pseudo-bases derived from benzthiazole alkyliodides, it is not possible to form mixed compounds by combination of a quaternary salt of benzthiazole with a quinaldinium salt. The thioisocyanines are powerful sensitisers for the green.[97]

NATURAL COLOURING MATTERS.

The synthesis of isohæmatein, identical with the product prepared from hæmatoxylin, is recorded. Veratrylidene-gallacetophenone-dimethyl ether (I.) in alcoholic solution is hydrogenated, by means of hydrogen in presence of palladious chloride, to 2-hydroxy-3.4-dimethoxyphenyl-β-veratrylethylketone (II.),



I. II.

which, on boiling with absolute formic acid and anhydrous zinc chloride, is converted into an isohæmatein tetramethyl ether salt

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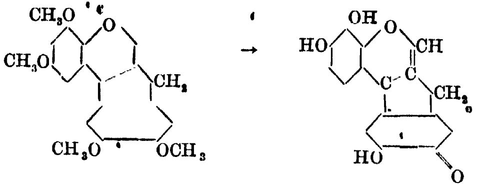
[95] W. H. Mills, *Chem. Soc. Trans.*, 1922, **121**, 455 ; *J.*, 1922, 365A.

[96] W. H. Mills and W. T. K. Braunholtz, *ibid.*, 1489 ; *J.*, 1922, 804A.

[97] W. T. K. Braunholtz and W. H. Mills, *ibid.*, 2004 ; *J.*, 1922, 997A.

(III.), which is isolated as the ferrichloride. Isohæmatein (IV.) is obtained from the latter by demethylation.[98]



III. IV.

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[98] H. G. Crabtree and R. Robinson, *Chem. Soc. Trans.*, 1922, **121**, 1033; *J.*, 1922, 582A.

FIBRES, TEXTILES, CELLULOSE, AND PAPER.

By Frank L. Barrett, A.I.C.,

Research Department, Tootal Broadhurst Lee Company, Ltd., Manchester.

A survey of the year's work leaves the gratifying impression that the application of science to industrial problems is becoming more general than has hitherto been the case. This is mainly due to the fact that the various Research organisations in this country and abroad are in active operation, and also to the very serious attempts being made in Central Europe and America to stabilise industries shaken by the war.

Details of the activities of the various British Research Associations may be gleaned from the Annual Report of the Privy Council for Scientific and Industrial Research,[1] and descriptions of the principal foreign Research Institutes have appeared in the technical literature from time to time. The remarks of P. Krais[2] on the aims of the German Textile Industry Research Institute of Dresden are worthy of special consideration.

Fibres—General.

An ingenious device for examining the behaviour of fibres under varying conditions of strain has been introduced by T. Barratt.[3] It consists, essentially, of a balance, to one arm of which the fibre is clamped, the other end being held in a clip attached to the central pillar. A known " pull " can be applied to the fibre by sucking a bundle of magnetised steel wires, attached to the opposite arm, into an electrically-controlled solenoid, movements of the balance arm being magnified about 200 times by means of a suitable arrangement of mirrors. It has been used in investigating the breaking strength, extensibility, and " recovery from strain " of various textile fibres, and has been successfully employed in examining the behaviour of these materials under the influence of different chemical reagents.

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[1] H.M. Stationery Office, 3s.

[2] *Chem.-Zeit.*, 1922, **46**, 856.

[3] *J. Text. Inst.*, 1922, **13**, 17T.

J. B. Vinckers[4] has investigated the amounts of torsion individual fibres can withstand, with the idea of throwing some light on their spinning properties. The results show that thin fibres may be twisted more often, before breaking, than thick ones of the same material. Attempts made to examine the brittleness of individual fibres and of yarns, by percussion tests, have been described by P. Krais.[5]

Important discussions on humidity, and its measurement, have taken place, and many forms of hygrometric apparatus have been described and discussed.[6] Attention may also be directed to the compilations of humidity-equilibria data, for various textile materials, given by R. E. Wilson and T. Fuwa.[7]

A preliminary observation of some interest is made by J. Huebner and J. M. Sinha,[8] who find that silk and wool, in common with certain cellulosic and other substances, yield iodoform when steam-distilled with iodine and sodium hydroxide.

COTTON.

The British Cotton Industry Research Association, whose admirably organised and well-equipped laboratories were formally opened in March, 1922,[9] is now actively engaged on the elucidation of many fundamental problems connected with the science and technology of cotton.

A considerable amount of important material, including a number of useful critical bibliographies, has been published by members of the Association's staff, through the medium of the *Journal of the Textile Institute.*

The subject of the structure and basic physical properties of the cotton hair is occupying the attention of investigators in this country and abroad, and it is to be hoped that the results obtained will throw light on the somewhat obscure nature of many of the treatments involved in the manufacture of the material.

Important contributions to our knowledge of the actual structure of the cotton fibre are made by W. L. Balls and H. A. Hancock,[10] who, in summarising the results of observations made subsequently to the discovery of growth rings in the cell wall,[11] draw conclusions concerning the actual structure of the individual growth rings, which are stated to be composed of spiral fibrils. The arrangement of these fibrillar components may determine the character of the extremely visible convolutions of the hair, and the cellulose aggregates composing each fibril may possibly have a definite geometrical conformation.

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[4] *Mededeel. Rijksvoorlicht. Vezel. Delft*, 1922, 21.

[5] *Text. Forschung*, 1922, **4**, 96.

[6] *Proc. Phys. Soc.*, 1922, **54**, i.-xcv., VIII.—XLIX.

[7] *J. Ind. Eng. Chem.*, 1922, **14**, 913 ; *J.*, 1922, 925A.

[8] *J.*, 1922, 93T.

[9] *J. Text Inst.*, 1922, **13**, 48T, 66T.

[10] *Proc. Roy. Soc.*, 1922, **B93**, 426.

[11] *Ibid.*, 1919, **B90**, 542.

The presence of convolutions in the cotton fibre is an important factor, having a bearing on the peculiar spinning properties of cotton; their precise function has been examined by A. Adderley,[12] in the course of an investigation of the clinging power of cotton hairs. The results obtained demonstrate the part played by the fibre convolutions in determining the strength and other properties of cotton yarn.

In the course of a study of flax, C. R. Nodder[13] compares the structural peculiarities of the cell wall of the cotton hair and the "dislocation marks" of flax. It is stated that flax and cotton fibres show a great similarity in structure, despite the fact that they are not botanically analogous.

Reference has already been made to the apparatus devised by T. Barratt, for examining the physical properties of fibres. Employing this instrument, he has determined the breaking stresses and extensions of a number of cotton hairs, and has correlated the results along with measurements of fibre lengths and diameters.[14] Detail, of a "group" method of testing the strength of fibres are given by E. D. Walen[15]; the strength of a group of fibres of known length, and weighing 1 gram, is determined, and calculated to a yarn number or equivalent figure.

Considerable attention has been devoted to the subject of the evolution of scientific methods of grading cotton. A simple method of conducting staple analyses is described by K. Berndt.[16] The same subject has been exhaustively dealt with by W. Frenzel,[17] who has applied mathematical and statistical treatments. He obtains the "fineness" of a sample of raw cotton, by dividing the weight of a number of fibres into their total length, recording the result in metres per gram, and makes recommendations concerning the application of the method to yarn examination.[18] In conjunction with J. H. Buskop,[19] he gives details, with graphs, of an exhaustive series of measurements made to determine the effect of various processes in the preparation of mule-spun yarn, on the average length of the fibres.

The relation between the heat developed by the action of caustic soda solution on cotton, and the strength of alkali employed, has been investigated by T. Barratt and J. W. Lewis.[20] Using a novel form of calorimetric apparatus, which enabled the heat generated to be measured directly, they find that the "heat of mercerisation" of cotton increases with the strength of lye used, but is not proportional to it. The commencement and progress of the mercerising action of the alkali are clearly demonstrated by the curve connecting these two factors.

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[12] *J. Text. Inst.*, 1922, **13**, 249T.

[13] *Ibid.*, 1922, **13**, 161, 213; *J.*, 1922, 853A.

[14] *Ibid.*, 1922, **13**, 220T.

[15] *Text. World*, 1922, **62**, 2017.

[16] *Text. Forschung*, 1921, **3**, 197. *Ibid.*, 1922, 429.

[17] *Mededeel. Rijksvoorlicht. Vezel Delft*, 1921, 7.

[18] *Ibid.*, 1922, 18.

[19] *Ibid.*, 1922, 41.

Investigations of the variation of fibre length following treatment of single cotton hairs with caustic soda solution under different conditions, have been made by R. S. Willows, T. Barratt, and, F. H. Parker.[21] The results, which afford an insight into the mechanism of mercerisation, tend to show that the action of caustic soda solution on cotton is much less rapid than is usually supposed, requiring up to three minutes (according to concentration) for its completion. At room temperature, with increase in the strength of alkali employed, axial contraction of the fibre increases rapidly, until a maximum is reached, when the concentration of the lye approaches 30° Tw. (sp. gr. 1·15). At 40° Tw. (sp. gr. 1·2) a minimum contraction is noted, while at 50° Tw. (sp. gr. 1·25) a second flat maximum developes, the contraction approaching zero as the concentration of the alkali reaches 86° Tw. (sp. gr. 1·43).

The temperature of the treatment is an important factor in determining the concentration at which contraction occurs, and in governing its periodical recurrence.[22] Graphical representations of the results of experiments at 0°, 18°, 45° and 85° C. show that one, two, three, and four well-defined maxima occur respectively. The concentrations at which contractions occur shift with increase in temperature, and at periods beyond each absolute maximum contraction there is a rapid decrease, which at 85° C. is most marked, and actually becomes an extension. The changes in sectional area and volume consequent on the treatment of cotton fibres with caustic soda solution, have been examined by R. S. Willows and A. C. Alexander.[23] They propose a simple test for the presence of tendered or damaged fibres, based on the observation that sections through the damaged portions, when treated with 30° Tw. caustic soda solution, swell abnormally in diameter without bulging at the ends, in contradistinction to normal material, where the restraining action of the cuticle causes an extrusion of swollen cellulose from the ends of the section. The probable structure of the cuticle of the cotton hair is discussed by R. Haller,[24] who supposes it to be produced by the adsorption of cutin substances by the cellulose. He has attempted to simulate the structure by producing copper ferrocyanide sheaths on rods of precipitated cellulose.

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[20] *J. Textile Inst.*, 1922, **13**, 113T.

[21] *Ibid.*, 1922, **13**, 229T.

[22] Private communication from R. S. Willows.

[23] *J. Text. Inst.*, 1922, **13**, 237T.

[24] *Text. Forschung*, 1921, **3**, 20; *J.*, 1921, 841A.

Potassium hydroxide is generally regarded as being inferior to the sodium compound in its mercerising action on cotton. It is suggested by P. Karrer, M. Staub, and A. Wälti[25] that the difference between the respective actions of the two alkalis is due to the fact that compounds of potassium hydroxide and cellulose are dissociated more easily than the analogous sodium hydroxide compounds. It is, therefore, necessary to employ more concentrated solutions of potassium than of sodium hydroxide, for obtaining comparative results.

E. de Menibus[26] gives details of determinations of moisture in various samples of raw cotton, and makes certain suggestions concerning a programme of work urgently required to be carried out on the subject. Investigations made by the Parks-Cramer Co.,[27] who have examined the moisture content of cotton at different stages of its manufacture, show that most of the moisture possessed by the raw material is lost in the opening process.

Removal of wax from cotton is stated to increase the strength of yarn prepared from it. Experiments made by the Cotton Research Co. of America, and recorded by C. E. Mead,[28] show this increase (which is probably due to a decrease in the tendency of fibres to slip one over the other) to be of the order of 15–20%.

Experiments on the effect of heat on cotton yarns are recorded by R. A. Truesdale,[29] who gives details of the conditions capable of bringing about a decrease in the strength of the material.

A somewhat novel process of preparing cotton for bleaching is protected by H. P. Bassett,[30] who subjects the material to weak acid and alkaline treatments, with intermediate and final washings. By these means the resinous and gummy impurities are hydrolysed and removed. Traces of residual organic acids are transformed to soluble salts by the action of the alkali.

Investigations of the variation in ash content of ozone-bleached cotton fabric subjected to laundering, have been made by P. Heermann and H. Sommer.[31] After 50 washes, the ash content rose from 0·38% in the case of the unwashed material, to 6·72% in the washed. Where the material was treated with detergents containing sodium silicate, very excessive amounts of ash (20–24·5%) were found. The laundering process included thorough final rinsings with soft and hard water.

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[25] *Helv. Chim. Acta*, 1922, **5**, 129.

[26] *Bull. Soc. Ind. Rouen*, 1921, **49**, 381, 547; *Rev. Gen. l'Ind. Text.*, 1922, **17**, 39.

[27] *Textile World*, 1922, **61**, 1541.

[28] *Ibid.*, 1921, **60**, 3501.

[29] *Text. Rec.*, 1922, **40**, 52.

[30] U.S.P. 1,402,040; *J.*, 1922, 139A.

[31] *Textilber.*, 1922, **3**, 238.

A method somewhat similar to that proposed by E. Knecht and L. Thompson[32] for determining the copper value of cotton is described by G. M. A. Koehler and M. Marqueyrol,[33] who, after treating the material with an alkaline solution of copper sulphate, estimate the cuprous oxide formed, by dissolving it in acid ferric sulphate solution, followed by titration of the ferrous salt produced with standard permanganate solution. The method is stated to give very concordant results.

A. F. Kitching[34] proposes to distinguish between cotton and wool by noting the difference in the fluorescence excited by exposure to ultra-violet light.

Methods for the analysis of cotton-asbestos mixtures are discussed by P. Heermann and H. Sommer,[35] who recommend a process based on the solubility of cotton in cuprammonium solution.

The observations of A. E. Oxley[36] and others on the examination of cotton yarn, and of H. F. Coward and G. M. Wigley[37] on the acidimetry and alkalimetry of cotton fabric, are reviewed elsewhere.

Preliminary notes on the destruction of the cotton hair by micro-organisms are published by H. J. Denham.[38] The communication is illustrated by interesting photomicrographs showing the degradation of fibres by bacteria and fungi, and accounts of their modes of attack are given.

WOOL.

The organisation and activities of the British Research Association for the Woollen and Worsted Industries are dealt with in the Annual Report of the Council of this organisation, a review of which has been published.[39]

The bulk of the Association's work has been assigned to three committees, dealing with research control, education, and sheep breeding, and the scheme of researches contemplated includes examination of the properties of the wool fibre, and investigation of several of the more important technical processes involved in its manufacture.

In order to stimulate pure research on several fundamental problems connected with the wool-consuming industries, the Association has awarded a number of Research Fellowships and

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[32] *J. Soc. Dyers and Col.*, 1920, **26**, 255.

[33] *Mém. Poudres*, 1921, **18**, 73 ; *J.*, 1922, 323A.

[34] *Analyst*, 1922, **47**, 206 ; *J.*, 1922, 525A.

[35] *Textilber.*, 1922, **3**, 340, 361, 382 ; see also *Mitt. Materialprüf.*, 1921, **39**, 315 ; *J.*, 1922, 745A.

[36] *J. Text. Inst.*, 1922, **13**, 54T.

[37] *Ibid.*, 1922, **13**, 121T ; *J.*, 1922, 497A.

[38] *Ibid.*, 1922, **13**, 240T.

[39] *J. Text. Inst.*, 1922, **13**, 68P.

Advanced Scholarships, tenable at various universities and technical colleges.[40] The precise scheme of operations with regard to inquiries into, and improvements in the breeding of sheep for wool production, is not outlined, but it is presumed that the experiments will be undertaken in conjunction with various agricultural colleges, and similar institutions interested in this subject.

The published information dealing with the economic production of wool and hairs for textile purposes, is rapidly accumulating, and our knowledge of this branch of the subject promises to be more complete than that of the actual chemical and physical characters of these fibres.

A. F. Barker[41] gives interesting details of fibre and staple analyses of wools from a number of sheep, selected from a typical Highland, Blackfaced flock. The use of frequency curves in the determination of staple-length, and the measurement and expression of fibre characteristics, have been dealt with by E. A. Fisher[42] and W. S. Holden[43] respectively.

F. A. E. Crew and J. S. S. Blyth,[44] in the course of a micrological study of the fleece of Blackfaced lambs, find that 50% of the fibres present in the case of fleeces from lambs which were still-born, or had died shortly after birth, presented the characters of normal wool; the remainder consisted of fibres of two kinds, which appear to represent transitions from hair to wool, in varying degrees. F. A. E. Crew[45] has also investigated the characters of the fleeces of certain primitive species of sheep.

According to E. Neumann,[46] experiments on the feeding of sheep with cystine preparations, by which means it is hoped to effect improvements in wool production, are in progress in Germany.

The subject of the physical properties of the wool fibre in its normal condition, or under the modifying influence of various reagents, is an important one, and it would appear that the form of apparatus used by T. Barratt, in his experiments on cotton, would be highly suitable for the carrying out of similar experiments on the wool fibre. Single merino wool fibres were found to be more than five times as extensible as fibres of scoured Egyptian cotton, and differed from the latter in their mode of recovery from strain.[47] A description of a projection apparatus, which has found application in wool testing, is given by W. Davis.[48] J. A. Hill[49] deals with

[40] *J. Text. Inst.*, 1922, **13**, 116P, 144P.
[41] *Ibid.*, 1922, **13**, 40T.
[42] *Text. Rec.*, 1922, **40**, 39.
[43] *J. Text. Inst.*, 1922, **13**, 157T.
[44] *Ibid.*, 1922, **13**, 17; *J.*, 1922, 626A.
[45] *Ann. App. Biol.*, 1921, **8**, 164.
[46] *Text. World*, 1922, **61**, 2955.
[47] *J. Text. Inst.*, 1922, **13**, 21T.
[48] *Wool Record*, 1922, **21**, 752.
[49] *Ibid.*, 1921, **20**, 1662.

the method employed by the University of Wyoming, for the determination of wool fibre diameters.

No new developments are to be recorded in connexion with the chemical aspect of the wool substance, with the isolated exceptions of the preliminary observations of J. Huebner and J. N. Sinha,[50] already referred to, and W. M Paddon,[51] who has shown that the amine groups of wool take no part in the dyeing of the fibre with certain acid colours. Experiments made at the Leeds University, to compare the value of skin wools with greasy fleece wools, and to determine the relative merits of sweated and sulphide-painted wools, recorded by K. O. Lefeaux and S. B. Hainsworth,[52] show that painted wool is superior to sweated wool, and is, in fact, practically equal to greasy wool for purposes of cloth manufacture.

Results of important investigations on the taking-up of neutral soaps by wool have been published by the British Research Association for the Woollen and Worsted Industries,[53] and serve to elucidate the functions of soap in the processes of scouring and soap-milling, substantiating in a very considerable measure the theory that the alkali of soap is the active agent in the milling process. The standard method employed by the Association for the determination of residual soap in wool, after submission to these processes, is described in detail[54]; it has been carefully worked out with reference to various factors, which may affect the accuracy of the estimations. Observations made during the treatment of wool for war purposes, by the French Government, throw some light on the efficacy of various methods of estimating scouring yields.[55]

"Protectol," a product of the Akt.-Ges. f. Anilinfabr., is stated to be an advantageous addition to various baths in the treatment of wool and allied substances.[56] In this connexion, attention may be directed to the various patents which have appeared, in which the use of carbohydrates, sulphite-cellulose waste liquors, and sodium lignosulphonate is claimed for this specific purpose. T. D. Smith protects the use of potassium alginate as a scouring agent.[57]

The patent literature contains accounts of several processes for improving the physical characters of hairs and wools, which appear to consist, mainly, of treatments with alkali sulphides or metallic salts. The use of solutions of alkaloids, alkaloid derivatives and decomposition products, for increasing the strength and elasticity of animal fibres, hairs, and feathers, is patented by J. Korselt.[58] The felting properties of hairs are stated to be improved by submission to the process of the Soc. Pichard Freres,[59] who subject the moistened material to intense cold, whereby disrupture of the fibres is effected. The use of colloids in milling is claimed by the Diamalt A.-G.[60]

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[50] *J.*, 1922, 93T.

[51] *J. Phys. Chem.*, 1922, **26**, 384 ; *J.*, 1922, 411A.

[52] *Wool Record*, 1922, **21**, 889, 961, 1033, 1105, 1177.

[53] *J. Text. Inst.*, 1922, **13**, 127T ; *J.*, 1922, 626A.

[54] *Ibid.*, 1922, **13**, 143T; *J.*, 1922, 626A.

[55] *Wool Record*, 1922, **21**, 1324.

[56] *Textilber.*, 1921, **2**, 353 ; *J. Soc. Dyers and Col.*, 1922, **38**, 126 ; *J.*, 1922, 197A.

[57] U.S.P. 1,405,560 ; *J.*, 1922, 248A.

S. R. Trotman[61] has examined the effect of chlorination on the physical and other properties of wool fibre, with special reference to the possibilities of damage arising, and its obviation. The tensile strength and elasticity of properly chlorinated wool are not impaired, but improper treatment results in weakening and a modification of several basic properties of wool; its affinity for dyes is increased, and it shows a tendency to wet more easily. The damage arising as the result of bad chlorination may be immediate, or take place during, or after, the finishing processes, if the removal of chlorine from the fibre is incomplete. It is caused by the destructive action of the chlorine, the disintegration being characterised by a breakdown of the cortical cells of the fibre, and disappearance of the epithelial scales. Hypochlorous acid is stated to be less dangerous than chlorine in its effect on the fibre, and it is therefore advantageous to employ the bleaching powder solution in such a manner as to minimise the liberation of free chlorine. This condition is obtainable when weak acids, such as boric or acetic acid, are used as souring agents. It is imperative *that the strength of the chlorinating solution should be governed by the character of the material to be treated.*

An interesting zoological study of the clothes moth (*Tineola biselliella*, Hum.), has been made by E. Titschack,[62] who finds that materials free from keratin are practically immune to the ravages of the insect. These researches, which included an examination of the behaviour of the moth towards a large number of materials, and an investigation of the effect of chemical reagents and physical conditions on the insect, its eggs, and larvæ, were carried out for F. Bayer u. Co., whose product, "Eulan," has been dealt with in the technical press.[63] This firm has protected a number of processes for the moth-proofing of wool, furs, and hairs, involving treatments with certain inorganic and organic acids and their salts.[64] Other patented preventives for the insect-proofing of animal products are dichloroethane[65] and α-tetrahydronaphthaleneketone.[66]

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[58] *E.g.*, G.P. 349,179 and 350,803; *J.*, 1922, 410A, 541A.
[59] E.P. 163,297; *J.*, 1922, 541A.
[60] G.P. 355, 104; *J.*, 1922, 747A.
[61] *J.*, 1922, 219T.
[62] *Z. tech. Biol.*, 1922, **10**, 1; *J.*, 1922, 892A.
[63] *Textilber.*, 1921, **2**, 350, 373.
[64] G.P. 344,266, 344,596, 347,723, 347,849; E.P. 173,536; *J.*, 1922, 289A, 521A, 139A.

R. O. Herzog[67] has evolved an ingenious method for the separation of cotton and wool fibres, based on the wetting properties of these materials. The process consists essentially in shaking the teased-out fibrous material with water and an immiscible liquid, such as a hydrocarbon or hydrocarbon derivative; the wool collects at the interface, and the cotton sinks in the water, from which it may be recovered.

Silk.

There are few developments to record in connexion with the chemical and physical aspects of the subject, though the biological side, associated with the economic cultivation of the silkworm (which does not come within the scope of this review), does not appear to have been quite so neglected. It may, however, be recorded that articles dealing with sericulture, and the development of the silk industry in the Argentine, Brazil, China, Colombia, Egypt, India, Italy, Roumania, San Salvador, Thrace, Turkey. and West Prussia, have appeared in the various technical journals Reports of the activities of the Sericultural Institutes at Bhagalpur[68] (India), Portici[69] (Italy), and at the University of Nanking[70] (China), have also been published. It is proposed to establish an International (American) Testing House for raw silk in Yokohama.[71]

The Silk Association of America make recommendations concerning the adoption of standards for raw silk classification, and propose four grades of material, the average physical characters of which are dealt with. W. F. Edwards[72] gives details of experiments to determine stress-strain relationships with special reference to the testing of raw silks. Two new instruments—the serimeter and serigraph—have been devised for silk testing. They have been designed to allow of an examination of the behaviour of the thread during loading, as this is considered to be of more importance than the usual determination of breaking strength and elongation.

K. Kondō[73] gives details of the preparation of alcohol-soluble and alcohol-insoluble sericin from silk. He gives result of an ultimate analysis of the alcohol-insoluble fraction, and also of an examination of the refractive indices of the two substances.

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[65] G.P. 353,682; *J.*, 1922, 747A.

[66] G.P. 357,063; J., 1922, 854A.

[67] G.P. 350,638; *J.*, 1922, 808A.

[68] *J. Ind. Ind. and Labour*, 1922, **2**, 116.

[69] *L'Italia Agricola*, 1921, **58**, 142.

[70] *Silk N.Y.*, 1922, **15**, 48.

[71] *Ibid.*, 1922, **15**, 68.

[72] *Amer. Silk J.*, 1921, **40**, 53; *Silk N.Y.*, 1921, **14**, 50; *Text. World*, 1922, **61**, 329, 1153.

[73] *J. Chem. Soc. Japan*, 1921, **42**, 1054.

Analyses of silk-fibroin, recorded by E. Abderhalden,[74] yielded amounts of *d*-alanine, *l*-leucine, phenylalanine, *l*-serine, and *l*-proline to the total extent of 31·8 grams per 100 g. of fibroin, 86·4% of the amino-acids being accounted for. At an intermediate stage of the hydrolysis, a compound, *d*-alanylglycine anhydride, was found to be present in quantity, along with small amounts of glycyl-*l*-tyrosine anhydride, and a third, unknown substance.

Of processes for the degumming and weighting of silk, there is nothing novel to record with the exception of the patent of L. M. Wohlgemuth,[75] who proposes to weight silk and other fibres with metals for which they have little or no affinity, by impregnating them with certain insoluble metallic hydroxides, or basic metallic silicates, followed by treatment with solutions of salts capable of forming adsorption compounds.

Bast and Other Vegetable Fibres.

The Linen Industry Research Association, whose headquarters are situated at Lambeg, near Belfast, commenced its scientific activities in March, 1920. A number of important investigations have been undertaken, several of which have been completed,[76] and communications from members of the Association's staff have appeared in the *Journal of the Textile Institute.* A somewhat similar organisation has been constituted in Germany; its laboratories at the Sorau Institute have been described by E. Schilling.[77]

Examination of the literature connected with the subject leaves the impression that the economic botany of fibre-yielding plants is receiving careful attention, especially abroad. In particular, several papers have appeared dealing with their scientific selection and breeding, and with the pathology of diseases common to plants of the flax type.

Observations on the structure of flax and allied fibres have been made by C. R. Nodder,[78] who finds that flax, ramie, hemp, and jute possess fibrillar structure, the components being arranged in spiral formation, so that these fibres may be regarded as having, to some extent, the structure of yarns. The spirals in flax and ramie are left-handed, whereas those in hemp and jute are right-handed; on moistening these fibres and allowing to dry in the air, flax and ramie twist in a clockwise direction, the twisting in the case of hemp and jute being in the reverse order. The opposite phenomena are noted on moistening, and these observations are put forward as a simple, but infallible test for distinguishing flax from its adulterants. It is suggested that a relationship may exist between the "dislocation marks" of flax, and the structural peculiarities—"stomata" and "slow spirals"— of cotton.

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[74] *Z. physiol. Chem.*, 1922, **120**, 207; *J.*, 1922, 539A.

[75] G.P. 312,301; *J.*, 1922, 289A.

[76] *J. Text. Inst.*, 1922, **13**, 162P.

[77] *Textilber.*, 1922, **3**, 118.

[78] *J. Text. Inst.*, 1922, **13**, 161T, 213T; *J.*, 1922, 853A.

The observations on the spiral structure of bast fibres, and on their behaviour on moistening and drying, are not entirely new, however. Somewhat similar conclusions have been published by H. Reimers,[79] and the distinctive test quoted above was proposed. Reimers states that this test is already known to a few experienced flax cultivators.

An optical method for the differentiation of flax and hemp is proposed by A. Herzog,[80] who, having unsuccessfully tried to employ determinations of refractive indices as a means of distinction, proposes a test based on the types of interference colours developed when these fibres are examined under the microscope, using a suitably arranged polariser with the interposition of a special selenite plate.

The fibres of true hemp (*Cannabis sativa*) are stated to differ from those of Sunn or Bombay hemp (*Crotalaria juncea*) in physical and structural characteristics, and in the colour and composition of the fibre ash. M. Pontio,[81] in discussing these differences, gives details of fibre measurements, colour reactions with iodine and sulphuric acid, and of the iron content of the various ashes, which enable a differentiation to be made. The nature of the terminal forkings of hemp fibres, which have been described and discussed at various times, is stated by W. Müller[82] to afford no data for locating their geographical origin.

New types of recording testing machines have been devised by J. A. Mathew[83] and G. F. New,[84] and have been applied to the examination of flax and other fibrous materials. These instruments, which are modifications of the Barr Autographic Wire Tester, have been chiefly employed for the examination of flax, in comparison with other yarns. The former observer has investigated the elastic properties of these materials, and the latter, who gives a number of stress-strain curves, develops a theory of the mechanism of yarn break. J. A. Mathew[85] has also given details of a simple but ingenious method of obtaining the apparent density of flax yarn, and discusses the relationship between this value, the count of the yarn, and its diameter.

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[79] *Textilber.*, 1921, **2**, 367, 381, 420.
[80] *Text. Forsch.*, 1922, **4**, 58.
[81] *Chim. et Ind.*, 1922, **7**, 664; *J.*, 1922, 458A.
[82] *Faserforsch.*, 1921, **1**, 246.
[83] *J. Text. Inst.*, 1922, **13**, 45T; *J.*, 1922, 212A.
[84] *Ibid.*, 1922, **13**, 25T; *J.*, 1922, 212A.
[85] *Ibid.*, 1921, **12**, 469T.

The probable modes of occurrence of pectic substances in plant tissues have been dealt with by D. H. F. Clayson, F. W. Morris, and S. B. Schryver,[86] who, in the course of a preliminary investigation, have examined the relation between pectinogen and pectin, and the properties of "cyclopectans" and "cyclopectic acids."

An interesting study of the pectic substances of flax has been made by E. Correns.[87] He has isolated these substances by the method of Bourquelot and Herrisey, and makes observations on the constituents of flax pectin with particular reference to the presence of an easily hydrolysable araban grouping and its components, the removal of which causes the dextro-rotation of flax pectin solutions to increase. The methoxyl contents of pectins varies with the treatments they have received, and the presence of these substances is supposed to influence the physical properties of the fibre. It is pointed out that the pectin content of material cannot be estimated on the assumption of a constant proportion of the methoxyl radicle being present.

Experiments made by M. H. Carré and D. Haynes[88] show that the precipitation of pectin as the insoluble calcium pectate ($C_{17}H_{22}O_{16}Ca$) can be used as an accurate method of analysis, if the conditions of the operation are carefully adjusted.

According to A. Herzog[89] it is not possible to apply microchemical colour reactions with ruthenium red and metallic salts to a macrochemical detection of the substance.

In continuing his researches on the taking up of iron solutions by plant tissues,[90] L. Rosenthaler,[91] in conjunction with F. Kolle, finds that the non-production of the Prussian blue reaction in certain cases, may be due to the presence of waxy cuticle, which prevents the absorption of liquids.

The use of acid solutions of benzidine hydrochloride as a reagent for the microchemical detection of lignified tissue, which it stains an orange colour, is dealt with by C. van Zijp,[92] who gives details of the technique of the process. A. R. Ling and D. R. Nanji[93] propose a modification of the well-known phenylhydrazine method for the determination of pentosans. After distilling off the furfuraldehyde in the usual manner and treating with excess of phenylhydrazine, followed by separation of the hydrazone, a known amount of iodine solution is added to the filtrate containing the residual phenylhydrazine (with which it reacts producing iodobenzene, hydriodic acid, and nitrogen), and the excess of iodine is back-titrated with sodium thiosulphate solution. By carrying out a blank titration with the original phenylhydrazine solution, and subtracting the titration figures in the two cases, the amount of furfuraldehyde in the distillate can be calculated.

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[86] *Biochem J.*, 1921, **15**, 643 ; *J.*, 1922, 75A.

[87] *Faserforsch.*, 1921, **1**, 229 ; *J.*, 1922, 366A.

[88] *Biochem J.*, 1922, **16**, 60 ; *J.*, 1922, 342A.

[89] *Faserforsch.*, 1921, **1**, 163.

[90] *Ann. Repts.*, 1921, **6**, 142.

[91] *Ber. deuts. pharm. Ges.*, 1921, **31**, 446.

[92] *Pharm. Weekblad*, 1921, **58**, 1539.

[93] *Biochem J.*, 1921, **15**, 466 ; *J.*, 1921, 752A.

The substitute fibre industry is still receiving attention on the Continent, and much research on the satisfactory commercial production of "imitation" products appears to be in progress in Germany, where, owing to the high price of imported commodities such as cotton, utilisation of the country's natural resources becomes an important factor. Communications have appeared in the German technical literature dealing with the subject of the production of spinnable fibres from a diversity of sources, and the preparation of cotton and wool substitutes. In these and other connexions, attention may be directed to the articles by S. Halen,[94] H. Schürhoff,[95] G. Kränzlin[96] and O. Johannsen,[97] and also to the address delivered by P. Krais,[98] previously referred to.

Various new fibres have been proposed for use in the production of textile materials. H. Guyot[99] gives details of the possible production of bast fibre from a species of rubber-yielding plant. Arghan,[100] a fibre of considerable length, obtained from a South American plant of the Maguey type, is stated to be a satisfactory substitute for cotton in the production of heavy canvases, and its cultivation is to be extensively undertaken in the East.[101] Fibres from the bark of the cotton stalk might be used for the replacement of the lower grades of jute, but their commercial exploitation seems very improbable on account of the high cost of separation.[102]

Little attention appears to have been directed to further investigations of the retting and allied processes; the patents connected with the subject are few in number. Investigations made in the Government Laboratory to determine the best method of disposing of ret liquors, to avoid river pollution, are recorded by A. J. H. Gauge.[103] They tend to show that partial purification may be effected by chemical precipitation methods, or by biological treatment on suitable filters, alternative treatments being the disposal on land, or discharge into sewers after neutralisation of acidity.

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[94] *Deuts. Faserstoffe*, 1922, **4**, 25.
[95] *Spinner u. Weber*, 1922, No. 11, 1.
[96] *Faserforsch.*, 1921, **1**, 121.
[97] *Textilber.*, 1922, **3**, 122, 149.
[98] *Chem.-Zeit.*, 1922, **46**, 856.
[99] *Textilber.*, 1922, **3**, 120.
[100] "*Manchester Guardian*" *Comml. Sup.*, 1922, July 5, 13.
[101] A. S. Moore, *Text. Rec.*, 1922, **40**, 43.
[102] *Bull. Imp. Inst.*, 1921, **19**, 13.
[103] *J.*, 1922, 177T.

The use of chlorine dioxide as a reagent for removing the incrusting substances of plants, proposed by E. Schmidt,[104] has been further examined by this investigator in collaboration with F. Duysen.[105] They deal with the application of solutions of this reagent in 50% acetic acid, in connexion with the microchemical examination of plant tissues.

ARTIFICIAL SILK.

It is of interest to note that important lectures on the artificial silk industry have been delivered during the year.

E. Bronnert,[106] of Strasbourg and Mulhouse, has addressed the members of the Society of Dyers and Colourists on the subject of "Progress in the Artificial Silk Industry," and C. F. Cross,[107] in a discourse before the Textile Institute, has reviewed the development and future of the production of artificial filaments for the textile industries. In the course of both these lectures, useful compilations of data concerning the production and properties of artificial fibres have been given.

The development of the artificial silk and staple fibre industries in Germany has been discussed by A. Lehne.[108] A number of new silks appear to have been introduced in this country, and various accounts of their apparently superior properties have appeared in the technical journals. Several of these products have been described by E. Neumann,[109] and E. Schülke.[110]

The cylindricity of artificial silk filaments is discussed by A. Herzog,[111] who, after reviewing the probable relationship between the forms of fibre cross-section and the physical properties of the materials, proposes, as a quantitative measure of their roundness, the ratio between the actual area of the cross-section and the area of a circle which would just enclose it. A new form of photometric glarimeter, described by H. Schulz,[112] has been employed for examining the gloss of artificial silks.

K. Hess,[113] in the course of an article on the scientific basis of artificial silk manufacture, emphasises the necessity for a thorough investigation of cellulose constitution as a starting point for improvements in the industry, making observations on the more recent work on cellulose constitution, and its bearing in this connexion. The probable transformations of cellulose complexes taking place during the manufacture of cellulosic filaments are discussed by W. Vieweg,[114] with special reference to the composition of the alkali-celluloses, and the nature of the xanthates capable of being spun; the latter are supposed to contain the complexes $(C_6H_{10}O_5)_3$ and $(C_6H_{10}O_5)_4$.

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[104] *Ann. Repts.*, 1921, **6**, 143 ; *J.*, 1921, 764A.
[105] *Ber.*, 1921, **54**, 3241 ; *J.*, 1922, 94A.
[106] *J. Soc. Dyers and Col.*, 1922, **38**, 153 ; *J.*, 1922, 540A.
[107] *J. Text. Inst.*, 1922, **13**, 167P.
[108] *Deuts. Faserstoffe*, 1922, **4**, 78.
[109] *Text. World.*, 1922, **61**, 2955.
[110] *Textilber.*, 1922, **3**, 174.
[111] *Text. Forsch.*, 1922, **4**, 99.
[112] *Deuts. Faserstoffe*, 1922, **4**, 85.
[113] *Textilber.*, 1922, **3**, 41.

The suitability, or otherwise, of wood and allied celluloses for artificial silk production is an important matter, and various methods of examination have been proposed. It has been stated, during a discussion in Germany,[115] that the necessary information may be readily obtained from micro-chemical investigations of their absorptive power for Malachite Green and the "corrosion" changes occurring on treatment with Congo-red and the zinc chloroiodide reagent.

C. G. Schwalbe and E. Becker,[116] in dealing with the behaviour of cellulose incrusting substances in the manufacture of viscose silks, give results of comparative analyses of these products and their parent substances. It is stated that in the case of silk prepared from wood cellulose, purification of the cellulosic material is effected by the viscose treatment, as evidenced by lower furfural yields and ash contents. In the case of silk prepared from cotton, however, the ash content of the product is greater than that of the parent material, and the hygroscopicity of the former is considerably increased.

The observations of E. Knoevenagel and H. Busch,[117] on the hydrolysis of viscose cellulose, are dealt with elsewhere.

The Plauson colloid mill[118] is now being manufactured in this country, and has been described by A. Forster and J. Reilly.[119] Its use in the manufacture of viscose solutions has been discussed by S. P. Schotz,[120] who deals with the formation of a particularly reactive alkali-cellulose by dispersing cellulose in the theoretical amount of aqueous caustic soda solution, and the production of the corresponding xanthates therefrom; this subject forms the basis of a patent taken out by H. Plauson,[121] who claims that by the employment of the apparatus, a viscose preparation requiring only very little ripening, may be rapidly and economically manufactured. A general description of impact and friction types of colloid mills and the ultra-filter press, with reference, amongst other uses, to their employment in viscose production, has been given by A. W. Kenney.[122]

[114] *Zellstoff u. Papier*, 1922, **2**, 18; *J.*, 1922, 541A.

[115] *Papierfabr.*, 1921, **19**, 1398.

[116] *Zellstoff u. Papier*, 1921, **1**, 168; *J.*, 1922, 367A.

[117] *Cellulosechem.*, 1922, **3**, 42; *J.*, 1922, 458A.

[118] *Ann. Repts.*, 1921, **6**, 126.

[119] *J.*, 1922, 435R.

[120] *Chem. Age*, 1922, **6**, 790.

[121] E.P. 184,533; *J.*, 1922, 806A.

[122] *Chem. and Met. Eng.*, 1922, **27**, 1080.

Numerous patents dealing with viscose silk manufacture have appeared, reference being made to the employment of various coagulating agents in the spinning bath (including compositions prepared from carbohydrates), to means for obviating undue degradation of the cellulose complex by shortening the time of "ripening" of the alkali-cellulose, and to methods for removing sulphur from the finished product, and recovering excess of carbon bisulphide.

C. C. L. G. Budde[123] proposes to employ a chemically-degraded cellulose for conversion to a product suitable for the manufacture of artificial filaments. Proposals to produce coloured viscose silks by incorporation of the leuco-compounds of vat and sulphur dyes with the alkali-cellulose or xanthate prior to spinning, are made by Courtaulds, Ltd., and L. P. Wilson.[124]

According to W. O. Mitscherling,[125] decomposition of viscose solutions can be prevented by the addition of 1% (calculated on the weight of cellulose present) of sodium thiosulphate.

The tendering of Chardonnet silk has been ascribed to the spontaneous liberation of free sulphuric acid from cellulose sulphates present in the material.[126] The detection and determination of free sulphuric acid and sulpho-acetates in cellulose acetates has been dealt with by M. Entat and E. Vulquin[127]; they recommend estimation of the free acid after extraction, or suitable hydrolysis, by an electrometric titration method. It is stated that all cellulose acetates prepared by methods in which sulphuric acid, or its derivatives, are used as catalysts, contain sulpho-acetates, but that the amount present does not exceed 0·03% (as sulpho-acetic acid) in the case of good quality products.

The amount of patent literature dealing with the preparation of ether and ester silks is relatively small, but contains a number of references to the dyeing of these materials.

Yarns and Fabrics.

The technical literature devoted to the subject contains numerous references to improvements in the sizing process, and to new methods for the analytical examination, and grading, of various sizing materials. Paraffin wax, which has long been regarded as an objectionable ingredient in size mixtures on account of the difficulties attending its subsequent removal from sized material, can, according to M. Fort,[128] be easily extracted by means of a suitable

[123] E.P. 184,610; *J.*, 1922, 806A.

[124] E.P. 181,902; *J.*, 1922, 627A.

[125] U.S.P. 1,415,040; *J.*, 1922, 459A.

[126] *Deuts. Faserstoffe*, 1922, 4, 78.

[127] *Ann. Chim. Analyt.*, 1922, 4, 131; *J.*, 1922, 541A.

[128] J. Soc. Dyers and Col., 1922, 38, 250.

extraction treatment with volatile solvents, which makes its general employment practicable.

Proposals to use rubber latex (which has been the subject of experiments in the paper industry[129]) for the sizing and finishing of textiles, have been dealt with by J. A. Hunter,[130] who states that research on its mode of application in these connexions is in progress.

A simple form of apparatus for testing the stiffness of sized fabric, in which varying lengths of material are allowed to protrude from a clamp fixed over a vertically-arranged piece of squared paper, has been devised by A. H. Grimshaw.[131] Measurements of the sagging of the strip can be made by reference to the graph paper, the method giving an indication of the ability of the cloth to sustain its own weight. It can be used for conducting experiments on the comparative stiffening values of various sizing materials.

The removal of sizing materials from yarns and fabrics is a matter of considerable importance and a fair amount of attention is being devoted to the subject, especially on the Continent, where new processes for the enzymic de-sizing of textiles have been evolved.

The use of animal amylases, applied in conjunction with neutral salts, to render these preparations less sensitive to high temperatures, and bile salts, to facilitate wetting, is protected by the Wyla-Werke G.m.b.H.[132] A. Boidin and J. Effront[133] propose to employ bacterial diastases for the removal of starchy, fatty, and gelatinous material present in textile goods. They claim that the diastatic secretions produced by *B. subtilis* and *B. mesentericus* are more stable and less sensitive to temperature changes than malt preparations, and possess an additional advantage in that they contain no fermentable carbohydrates.

The combined use of proteolytic and diastatic enzymes for the purification of yarns and fabrics is claimed by J. Takamine and J. Takamine, jun.[134]

A number of papers published on the subject of starch-splitting enzymes may have direct bearing on problems connected with the removal of foreign matter from textile materials, in that careful regulation of the conditions of action is necessary, and the possible effect of foreign substances must be taken into account, if the satisfactory working of such delicately adjusted reactions as those of an enzymic character is to be ensured.

[129] F. Kaye, *Indiarubber J.*, 1922, **64**, 435; *J.*, 1922, 806A.

[130] *Text. World*, 1922, **62**, 3014.

[131] *Ibid.*, 1922, **61**, 2965.

[132] G.P. 359,597.

[133] G.P 349,655.

[134] U.S.P. 1,421,613; *J.*, 1922, 627A.

The diastatic power of malt is stated to be three to four times that of its commercial preparations.[135] The conditions governing the operation of the starch-amylase system have been exhaustively examined by H. Luers and W. Wasmund.[136] J. Effront,[137] who proposes a method for determining the activity of amylases based on the coagulating action of iodine on starch paste, has also given details for the characterisation of these products.[138]

Studies of the toxic action of various substances on amylases have been made by H. C. Sherman and M. Wayman,[139] and also by U. Olsson.[140] The former investigators find that toluene has little effect on natural or purified amylases of animal or vegetable origin, but that the preparations are injured by formaldehyde, and are very sensitive to copper salts. The latter observer states that whereas the effect of copper salts is gradual, an immediate inhibitive effect is exerted by silver compounds. According to H. C. Sherman and M. L. Caldwell,[141] the toxic effect of copper sulphate on amylases may be prevented, and even counteracted, by the addition of certain amino-acids, which are also stated to increase the activity of the enzymes, and prevent their deterioration in the aqueous dispersion in which they act.

Observations which might be investigated from the standpoint of textile de-sizing have been made by T. Isawa,[142] who finds that the presence of sodium oleate retards the amylolytic digestion of soluble starch, the soap acting as a protective for the carbohydrate, and by J. Effront,[143] who has noted that filter paper adsorbs ptyalin, which is not readily removed from it. Researches into the effect of traces of metallic salts, soaps, waxes, and other ingredients of size mixtures, which may possibly survive the treatments preliminary to enzymic de-sizing, and the possible selective removal of enzyme from the de-sizing bath by the fabric during treatment, might lead to considerable increases in the efficiency of this important process.

The presence of residual sizing materials in textile fabrics, or of carbohydrates introduced as fillers during the final stages of their manufacture, is often responsible for the development of bacterial or fungal defects arising during their subsequent storage or overseas transportation, in that suitable and easily assimilable food materials are provided which favour the growth of micro-organisms. A considerable amount of work on the rendering of such filling materials antiseptic still remains to be carried out; in a general connexion, attention may be directed to the observations of H. v. Euler and O. Svanberg,[144] on the conditions favouring the decomposition of starch by *B. macerans*, and of E. J. Sidebotham,[145] who traced the discoloration of a piece of cotton fabric to the presence of a fungus (*Botrytis*) occurring in the wood of the wrapping board.

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[135] *J. Pharm. Chim.*, 1922, **25**, 18.
[136] *Fermentforsch.*, 1922, **5**, 169.
[137] *Comptes rend. soc. biol.*, 1922, **86**, 269.
[138] *Comptes rend.*, 1922, **174**, 18; *Comptes rend. soc. belge de biol.*, 1922, 12.
[139] *J. Amer. Chem. Soc.*, 1921, **43**, 2454.
[140] *Z. physiol. Chem.*, 1921, **114**, 51.
[141] *J. Amer. Chem. Soc.*, 1921, **43**, 2461.
[142] *J. Med. Soc. Kyoto*, 1921, **18**, 49.
[143] *Comptes rend. soc. belge de biol.*, 1922, **9**.

New methods for the physical testing of yarns and fabrics continue to be evolved. The modifications of the Barr testing machine, used by J. A. Mathew[146] and G. F. New,[147] have already been referred to; these instruments should be useful for the examination of all classes of yarn. Apparatus described by W. F. Edwards,[148] for investigating stress-strain relationships in silk threads, should also find more general application.

Articles describing new types of textile testing machinery have appeared in the various technical journals. The Scott tester,[149] an instrument possessing many novel features, is being fairly extensively used in America. The Buskop tearing tester,[150] a device for attaching to the standard Schopper machine, enables measurements to be made of the load required to bring about tearing of fabric under standard conditions.

Instruments for determining the degree of regularity of the "hardness" and evenness of yarn have been devised by A. E. Oxley[151] and E. D. Walen,[152] the principles employed being very similar in each case. In the former investigator's apparatus, the yarn is drawn between case-hardened shoes, the lower being fixed and the upper movable. The movement of the upper shoe, due to irregularities in the yarn, is greatly magnified and recorded photographically on a band of sensitised paper, the movement of which is synchronised with that of the yarn. The design of the apparatus presents considerable ingenuity, and the results obtained, which throw some light on the character of yarn structure and the conditions obtaining during spinning, afford an excellent example of the employment of scientific method in textile investigation.

A different, but equally ingenious type of continuous yarn regularity tester has been devised by W. Frenzel.[153]

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[144] *Biochem. Zeits.*, 1922, **128**, 323.

[145] *J. Soc. Dyers and Col.*, 1922, **38**, 97; *J.*, 1922, 366A.

[146] *J. Text. Inst.*, 1922, **13**, 45T; *J.*, 1922, 212A.

[147] *Ibid.*, 1922, **13**, 25T; *J.*, 1922, 212A.

[148] *Silk N.Y.*, 1921, **14**, 50; *Text. World*, 1922, **61**, 329, 1153.

[149] *Text. World*, 1921, **60**, 3006.

[150] *Med. Rijksvoorlicht. Vezel. Delft*, 1922, 35.

[151] *J. Text. Inst.*, 1922, **13**, 54T.

[152] *Text. World*, 1922, **62**, 3177.

[153] G.P. 353,086; *Leip. Monats. Text.-Ind.*, 1922, **37**, 166.

Communications dealing with the actual testing of materials are few in number. J. Huebner,[154] in the course of an account of researches on the effect of scouring and bleaching on the structure and strength of cotton fabrics, points out that the results obtained by withdrawing and testing single threads from cloth are not directly comparable with tensile strength and ripping tests made on the material.

The effect of heat on the tensile strength and other properties of cotton, linen, and ramie yarn has been dealt with by R. A. Truesdale.[155] R. Truesdale and C. Hoyes [155a] propose radiographical methods for the examination of the effect of various treatments subsequent to its manufacture, on canvas, the surface of which has been obliterated by impenetrable fillings. The fibres from which the material is manufactured are rendered opaque to X-rays by precipitating lead chromate upon them.

The introduction of instruments for quantitatively examining the gloss on paper has led to consideration of their possible utility in textile work for the measurement of lustre. The best known of these instruments, the Ingersoll glarimeter,[156] operates by determining the proportion of light polarised by oblique reflection from a glossy surface.

The use of the polarisation glarimeter in textile work is dealt with by K. Kieser.[157] Another type of instrument embodying the use of a photometer, has been described by H. Schulz[158]; it has found application in artificial silk testing. W. Douglas[159] gives details of a half-shade photometer for measuring the degree of whiteness of a fabric, the material under examination being compared with a standard of chemically pure barium sulphate.

Attempts have been made to devise methods whereby a quantitative expression of the wearing properties of fabrics may be determined. E. Muller[160] gives details of an apparatus for carrying out rubbing tests on cloth, the material under examination being clamped (with or without tension) on a plane surface, and an adjustably loaded rubbing surface reciprocated over it by means of a suitable motor drive. S. A. van Hoytema[161] describes experiments made to determine the wearing properties of carpets and mats; the loss of weight of the material was noted after rubbing on a revolving grindstone under standardised conditions.

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[154] *J. Soc. Dyers and Col.*, 1922, **38**, 29; *J.*, 1922, 213A.

[155] *Ann. Repts.*, 1921, **6**, 123.

[155a] *J. Text. Inst.*, 1921, **12**, 418; *J.*, 1921, 882A

[156] *Paper*, 1921, **29**, Oct. 26.

[157] *Deuts. Faserstoffe*, 1922, **4**, 1.

[158] *Ibid.*, 1922, **4**, 85.

[159] *Textilber.*, 1921, **2**, 411.

[160] *Text. Forschung*, 1922, **4**, 95.

[161] *Leip. Monats. Text.-Ind.*, 1921, **36**, 201.

The thermal conductivity of wearing fabrics has been investigated by E. S. Rood,[162] who, employing the disc method of Lees with suitable corrections, has measured the conductivity of knitted and woven cotton, woollen, silk, and linen materials. The results obtained show the values to be greater: (*a*) for dense than for loosely knitted or woven material; (*b*) for several layers than for a few; (*c*) for moist than for dry material.

Reference has already been made to published collections of humidity-equilibria data[163] for fibres and fabrics; several communications on the hygrometric properties of textile materials have appeared in the literature. In particular, attention may be directed to the observations of R. Kimura,[164] who, in investigating the water-absorbing properties of fabrics from the point of view of "airing," obtains results very similar to those previously noted by A. Scheurer.[165]

The dangers of traces of acid remaining in fabric have been emphasised by J. B. Vinckers,[166] who refers to the difficulty of estimating small amounts of acid in cloth. The observations of H. F. Coward and G. M. Wigley[167] will therefore be welcomed. These investigators, who have made a careful study of the acidimetry and alkalimetry of bleached cotton fabric, find that small amounts of acid or alkali present in the material can be determined by titration with $N/50$ solutions at the boil, and in presence of the cloth. By this means, accurate estimations, correct to 0·01% of HCl (or H_2SO_4) or 0·02% NaOH (present as Na_2CO_3), can be made. They make very useful recommendations concerning the employment of certain indicators for the approximate determination of the acidity and alkalinity of textile materials. The effect of acid treatment on the strength of cellulosic materials has been dealt with by H. Alt.[168]

Numerous processes for the waterproofing and fireproofing of fabrics continue to be introduced, but the majority present no specially novel features. In the Tate process,[169] however, a novelty is introduced in that a waterproofing, which is stated to be superior in many respects to those obtained by the older methods, is effected by the electro-deposition of insoluble aluminium compounds within the fabric.

[162] *Phys. Rev.*, 1921, **18**, 356.
[163] *J. Ind. Eng. Chem.*, 1922, **14**, 913; *J.*, 1922, 925A.
[164] *Arch. Hyg.*, 1922, **91**, 183.
[165] *Ann. Repts.*, 1921, **6**, 113; *J.*, 1921, 539A.
[166] *Med. Rijksvoorlicht. Vezel, Delft*, 1922, 26.
[167] *J. Text. Inst.*, 1922, **13**, 121T; *J.*, 1922, 497A.
[168] *Textilber.*, 1921, **2**, 430.
[169] H. J. M. Creighton, *J. Franklin Inst.*, 1921, **192**, 497; 1921, 842A.

CELLULOSE.

General.

The publication of the fourth volume of the series of collected "Researches on Cellulose," originally undertaken by C. F. Cross and E. J. Bevan, will be welcomed.[171] It has been compiled by C. F. Cross and C. Dorée, and contains an excellent critical review of the more important papers appearing during the period 1910–1921, special attention having been paid to the presentation of comparatively full abstracts of papers published in journals which are not readily accessible. It will find a prominent place in the libraries of all cellulose chemists and technologists.

Physical and Colloid Properties.

Investigations of the moisture content of numerous carbohydrates, including cellulose, under different conditions of atmospheric humidity, have been made by C. A. Browne[172]; owing to the operation of conditions affecting the course of the experiments, no fixed relationship between this property and the percentage humidity of the atmosphere could be established.

In dealing with the heat of combustion of cellulose, F. O. H. Binder[173] compares the results obtained by calculation using the Dulong formula, and a modification thereof, with those given by Muspratt. Employing a new method of calculation, he obtains a value of 4182 calories, Muspratt's experimental value being 4189 calories.

Reference is made by C. F. Cross and C. Dorée[174] to systematic investigations of specific volumes of cellulose and its derivatives, carried out in the laboratory of Messrs. Courtaulds, Ltd., in association with S. J. Lewis, who, in the course of his experiments, noted abnormal phenomena, which are being carefully examined.

This investigator, in continuing his important work on the fluorescence of cellulose,[175] has obtained results which, represented graphically, define the relationships between the fluorescent powers of a number of substances of animal and vegetable origin, and the wave-lengths of the incident light.[176] Results obtained during an examination of celluloses and sugars indicate that some relation between structure and fluorescent power may probably exist.

In connexion with the fluorescent properties of various substances, attention may be directed to the observations of A. F. Kitching.[177]

[171] Longmans, Green and Co.
[172] *J. Ind. Eng. Chem.*, 1922, **14**, 712; *J.*, 1922, 723A.
[173] *Chem.-Zeit.*, 1921, **45**, 141.
[174] "*Researches on Cellulose*," Vol. 4, p. 22.
[175] *Ann. Repts.*, 1921, **6**, 124.
[176] *J. Soc. Dyers and Col.*, 1922, **38**, 68, 99; *J.*, 1922, 366A.
[177] *Analyst*, 1922, **47**, 206; *J.*, 1922, 525A.

Experiments on the electro-endosmose of organic liquids through a cellulose (filter paper) membrane have been made by A. Strichler and J. H. Mathews,[178] who give consideration to the various factors influencing the establishment of its original charge.

The supposed adsorption of alumina by cellulose has been examined by A. Tingle,[179] who states that its apparent withdrawal from solutions of aluminium salts is due to chemical precipitation by non-cellulose impurities invariably present. Reference has already been made to the observations of J. Effront,[180] who finds that filter paper adsorbs ptyalin, which only passes into solution again in presence of sodium chloride or starch paste.

The significance of the colloid character of filter paper, with special reference to adsorption effects in relation to analytical operations, is discussed by H. Bassett.[181]

It is well known that cotton exhibits preferential attraction for the cations of certain neutral salts in aqueous solution. H. Masters[182] finds that the acidity and alkalinity developed, respectively, on treating carefully purified cotton with solutions of sodium chloride and other neutral salts, and on extracting the treated material with water, can be estimated by simple titration methods, and are proportionally equivalent. The results of these experiments are of interest in the light of work already published on the mechanism of neutral salt reactions.

As pointed out in last year's Report, important researches on the solvent action of aqueous solutions of neutral salts on cellulose have been carried out by H. E. Williams.[183] The theoretical aspect of this subject has been dealt with in a subsequent publication.[184]

The character of the solvent action of cuprammonium and copper-ethylenediamine solutions on cellulose has been exhaustively examined by W. Traube.[185] The reaction between metal-base complexes and polyhydroxy compounds is one of alcoholate formation, but the dissolution of cellulose in cuprammonium solution can hardly be explained on this fact alone; the copper complex has a specific action on cellulose, bringing about an essential primary degradation. The probable mechanism of the solvent action of the copper-ammine hydroxide solutions is discussed in the light of observations made on the reaction between copper-ethylenediamine hydroxide and glycerol.

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[178] *J. Amer. Chem. Soc.*, 1922, **44**, 1647.

[179] *J. Ind. Eng. Chem.*, 1922, **14**, 198; *J.*, 1922, 289A.

[180] *Comp. rend. Soc. belge de biol.*, 1922, 9.

[181] *4th Report on Colloid Chemistry*, 1922, p. 15.

[182] *Chem. Soc. Trans.*, 1922, **121**, 2026.

[183] *J.*, 1921, 221T; *Ann. Repts.*, 1921, **6**, 127.

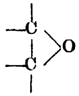
[184] *Mem. Manchester Lit. Phil. Soc.*, 1921, **65**, 12; "*Researches on Cellulose*," *Vol.* 4, p. 48.

[185] *Ber.*, 1921, **54**, 3220; *J.*, 1922, 97A; *Ber.*, 1922, **55**, 1899.

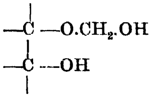
Conclusions very similar to those of Traube concerning the constitution of the copper-cellulose complex have been reached by K. Hess and E. Messmer[186] in the course of a continuance of their work on the optical activity of cellulose in cuprammonium solutions.[187] It is considered that the copper-cellulose ratio in the soluble complex is most usually in the order of $1Cu : 2C_6H_{10}O_5$, but that multiples other than 1 : 2 are possible. The ratio 1 : 2 is, however, supported by the composition of the cellulose-copper-sodium hydroxide complex, which has been determined, and is found to be $Na_2(C_{12}H_{16}O_{10}Cu)$.

The work of W. H. Gibson, L. Spencer, and R. McCall[188] on the viscosity of cellulose in cuprammonium solution has attracted other investigators to this field. M. Nakano, who has previously used the hydrogen capillary viscosimeter in an examination of the effect of heat and mercerisation on cellulose,[189] proposes a modification of this instrument,[190] and a new form of falling sphere viscosimeter[191] has been described by R. A. Joyner, who has made a careful and exhaustive investigation of the factors affecting viscosity determination,[192] and the effect of various reagents on the lowering of the viscosity of cellulose.[193]

A paper of considerable interest in connexion with the Sthénose treatment of artificial silks[194] has been contributed by M. Samec and S. Ferjančič.[195] Cellulose, in the form of an emulsoid in sulphuric acid, is stated to react with formaldehyde, addition probably taking place through the opening of an oxygen ring of the type



and the formation of an oxymethylene group



$$\begin{array}{l} -\overset{|}{C}-O.CH_2.OH \\ -\underset{|}{C}-OH \end{array}$$

Constitution.

The employment of strictly physical methods of examination, in attempts to elucidate organic chemical constitution, is a somewhat new and interesting venture. Unfortunately, in the past, there has been very little co-operation between the pure organic chemist and the physicist, but it is to be hoped that time will change this; the more recent developments in atomic and molecular physics have done much to demonstrate the importance of physical considerations in relation to molecular structure, and the possible utility of the physicist in the realms of structural organic chemistry.

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[186] *Ber.*, 1922, **55**, 2432 ; *J.*, 1922, 892A.
[187] *Ann. Repts*,, 1921, **6**, 128.
[188] *Ibid.*, 1921, **6**, 126.
[189] *Ibid.*, 1921, **6**, 114.
[190] *Kogyo-Kwagaku Zasshi*, 1921, **24**, 1395 ; *J.*, 1922, 366A.
[191] *Chem. Soc. Trans.*, 1922, **121**, 1511 ; *J.*, 1922, 806A.
[192] *J.*, 1922, 276R.
[193] *Chem. Soc. Trans.*, 1922, **121**, 2395 ; *J.*, 1923, 90A.
[194] *Ann. Repts.*, 1917, **2**, 136.
[195] *Koll. Chem. Beihefte*, 1921, **14**, 209 ; *J.*, 1922, 94A.

During recent years, very serious attempts have been made to apply X-ray spectrographic methods to the examination of various complex substances of animal and vegetable origin, with the idea of obtaining precise information concerning the structural characteristics of their ultimate components. The greater portion of this work, to which attention may be directed, has been published in the *Zeitschrift für Physik*.

As a result of several of these investigations, R. O. Herzog[196] puts forward a number of interesting if somewhat speculative theories. He assumes that the symmetry of the rhombic or possibly of the monoclinic crystal system, is represented in the cellulose molecule, and suggests arrangements of dextrose or cellobiose residues which may occur in its structure, three possible types being dealt with in detail.

Our knowledge of the chemistry of the carbohydrates in general, and the polysaccharides in particular, increases steadily. It is being continually enriched by the valuable communications from the laboratories of the St. Andrews University, and by the researches of the various well-known Continental investigators. Many of the results so far recorded have been somewhat contradictory, and have occasioned much discussion, but there is no doubt that important fundamental information is being rapidly amassed, and that we are approaching the real solution of cellulose and higher polysaccharide structure.

Exhaustive examinations of several of the mono- and disaccharides have been made, and new derivatives of a number of these substances have been prepared. The oxidational and other degradations of dextrose have formed the subject of much careful study, and a fairly thorough knowledge of the character of several of the products formed has resulted.

Of investigations on substances closely allied to cellulose, attention may be directed to those made on starch and inulin.

The polyamyloses, products of the bacterial degradation of starch, continue to occupy the attention of P. Karrer and his co-workers.[197] Evidence is adduced that triamylose is identical with β-hexa-amylose,[198] and is therefore a polymerised anhydromaltose, the unit of starch being regarded as a simple anhydromaltose. This latter view, however, is contrary to that held by other workers, especially by A. Pictet, who, in conjunction with R. Jahn,[199] has obtained a new depolymerisation product (provisionally called "trihexosan") by heating potato starch in glycerol, this substance being produced to the extent of 90% of the weight of the original starch, and J. C. Irvine, who, with other collaborators, proposes new formulæ for starch and cellulose. In conjunction with J. Macdonald, he puts forward the theory, based on observations made on the methylation and subsequent hydrolysis of purified rice starch, that the starch unit in this case is a trihexosan, and that it may be represented by the following formula (I.).[200]

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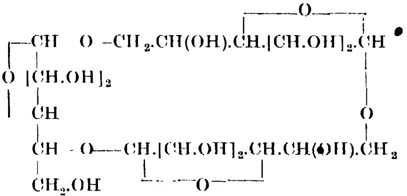
[196] *Cellulosechem.*, 1921, **2**, 101; *J.*, 1922, 8A.

[197] *Helv. Chim. Acta*, 1922, **5**, 181; *J.*, 1922, 304A.

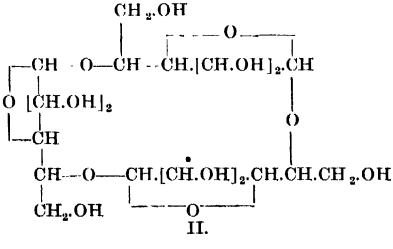
[198] *Ber.*, 1922, **55**, 2854; *J.*, 1922, 910A.



I.

Attention may now be drawn to his more important remarks (from the point of view of this report) on cellulose.

Consideration of the results obtained by W. S. Denham in his researches on the methylation of cellulose,[201] and a subsequent examination of 2.3.6-trimethylglucose,[202] produced as a result of the hydrolysis of products of the reaction, has led him, along with W. S. Denham and E. L. Hirst,[203] to propose a somewhat similar formula for cellulose (II.), in the evolution of which, more recent work on the hydrolysis of methylated cellulose, and the nature of the yield of cellobiose obtainable by cellulose acetolysis, was taken into account.



II.

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[199] *Helv. Chim. Acta*, 1922, **5**, 640 ; *J.*, 1922, 871A.
[200] *British Association Reports*, 1922, **B**, 16.
[201] *Chem. Soc. Trans.*, 1921, **119**, 77.
[202] *Ibid.*, 1922, **121**, 1213 ; *J.*, 1922, 723A.
[203] *British Association Reports*, 1922, **B**, 10.

It may be of interest to note that J. C. Irvine, E. S. Steele and M. I. Shannon[204] have established the fact that inulin is composed entirely of γ-fructose residues, and a formula based on their observations now remains to be put forward. Determinations of the molecular weight of inulin triacetate, which was found to be about 2600, led H. Pringsheim and M. Lassmann[205] to suppose that inulin contains nine fructose residues. Its unit is stated to be anhydro-tri-fructose.[206] Other formulæ for starch and cellulose have been proposed by J. J. Lynst Zwikker,[207] and subsequently amended.[208]

The acetolysis of cellulose still receives much attention. In continuation of earlier work,[209] J. C. Irvine and E. L. Hirst,[210] using W. L. Barnett's process[211] for the preparation of the cellulose triacetate employed in the experiments, obtain results which confirm earlier observations[212] and establish the fact that cotton cellulose is composed entirely of glucose residues. Cello*iso*biose, a disaccharide previously isolated from the products of cellulose acetolysis by H. Ost and R. Prosiegel,[213] has been the subject of further examination by the former investigator, in conjunction with G. Knoth.[214]

K. Hess,[215] in the course of experiments on the degradation of cellulose with acetyl chloride, has obtained as a final product, a new (hexa-acetyl) anhydro-biose; this substance, while possessing many of the properties of the sugars, has some of the characters of normal cellulose. P. Karrer has continued earlier work on the degradation of cellulose to brominated sugars,[216] and as the result of experiments made in collaboration with A. P. Smirnoff,[217] makes deductions concerning the possibility of the cellulose unit being a polymerised anhydro-cellobiose (cellosan). Similar conclusions were arrived at in the course of a discussion of the probable constitution of alkali-celluloses.[218]

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[204] *Chem. Soc. Trans.*, 1922, **121**, 1060; *J.*, 1922, 603A.

[205] *Ber.*, 1921, **54**, 1281; 1922, **55**, 1409; *J.*, 1922, 513A.

[206] *Ber.*, 1922, **55**, 1414; *J.*, 1922, 513A.

[207] *Rec. Trav. Chim.*, 1922, **41**, 49; *J.*, 1922, 152A.

[208] *Ibid.*, 1922, **41**, 152; *J.*, 1922, 305A.

[209] *Ann. Repts.*, 1921, **6**, 132.

[210] *Chem. Soc. Trans.*, 1922, **121**, 1585; *J.*, 1922, 745A.

[211] *Ann. Repts.*, 1922, **6**, 139.

[212] *Cf.* G. W. Monier-Williams, *Chem. Soc. Trans.*, 1921, **119**, 803; *J.*, 1921, 539A.

[213] *Z. angew. Chem.*, 1920, **33**, 100; *J.*, 1920, 421A.

[214] *Cellulosechem.*, 1922, **3**, 25; *J.*, 1922, 409A.

[215] *Ber.*, 1921, **54**, 2867; *J.*, 1922, 9A.

[216] *Ann. Repts.*, 1921, **6**, 132.

[217] *Helv. Chim. Acta.*, 1922, **5**, 187; *J.*, 1922, 305A.

[218] *Cellulosechem.*, 1921, **2**, 125; *J.*, 1922, 170A; *cf.* *J.*, 1922, 188A.

The chemistry of lævoglucosan (β-glucosan) does not appear to have progressed appreciably. A study of its polymerisation has been made by A. Pictet and J. H. Ross.[219]

Cellulose Degradation Products.

In view of a possible world shortage of liquid fuel, the subject of the utilisation of cellulosic materials for the production of power alcohol becomes an important one. A review of the technical processes for the hydrolytic conversion of cellulose to fermentable sugars has been published by P. P. Budnikow and P. W. Solotarew,[220] who have made experiments with the idea of devising an efficient process for the hydrolysis of cellulose, with special reference to methods for the removal of acid prior to fermentation.

Extensive remarks on the properties of modified celluloses have been made by E. Knoevenagel and H. Busch.[221] Regenerated (viscose) and heat-degraded celluloses are converted into alkali-soluble modifications by suitable treatment with hydrochloric acid gas. Their work is discussed by E. Heuser and W. von Neuenstein.[222] E. Heuser[223] regards oxycellulose as an impure cellulose containing small quantities of an oxidation product in intimate association with it, and in collaboration with F. Stöckigt,[224] proposes methods for the analytical examination of degraded celluloses.

The relation between the amount of oxidant used in the oxidation of cellulose, and the copper value of the product, has been examined by E. Knecht and F. P. Thompson,[225] who find that after a half-atomic proportion of oxygen has been utilised, the rise in the copper number is gradual. They have also investigated the acetylation and nitration of oxidised cellulose, and conclude that oxidation affects the activity of the hydroxyl groups of cellulose.

According to E. Justin-Mueller,[226] hydrocellulose may be distinguished from oxycellulose and normal cellulose, in that it turns yellow and caramelises at a much lower temperature than these substances.

The preliminary observations of J. Huebner and his co-workers are of interest, and one awaits further results. On steam-distilling cellulose with iodine and caustic soda, iodoform is produced[227]; also, it has been noted that purified cellulose, on exposure to water or water vapour at 35° C. for a considerable time, yields traces of soluble aldehydes.[228] These phenomena are being carefully investigated, and may throw some light on the nature of cellulose degradation.

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[219] *Comptes rend.*, 1922, **174**, 1113 ; *J.*, 1922, 428A.

[220] *Ber. Polyt. Iwanowo-Wosniessensk*, 1921, **4**, 119 ; *J.*, 1922, 745A.

[221] *Cellulosechem.*, 1922, **3**, 42 ; *J.*, 1922, 458A.

[222] *Ibid.*, 1922, **3**, 89, 101.

[223] *Papierfabr.*, 1921, **19**, 1393.

[224] *Cellulosechem.*, 1922, **3**, 61 ; *J.*, 1922, 583A.

[225] *J. Soc. Dyers and Col.*, 1922, **38**, 132 ; *J.*, 1922, 497A.

[226] *Bull. Soc. Chim.*, 1921, **29**, 987 ; *J.*, 1922, 9A.

[227] *J.*, 1922, 93T.

The subject of cellulose fermentation still continues to occupy the attention of the various Continental workers. Papers, too numerous to mention in detail, have appeared, the subject having been examined from the points of view of plant pathology and metabolism, and soil chemistry.

In continuing his observations on the properties of selenium oxyhalides, V. Lenher[229] has prepared selenium oxybromide, and finds that, in common with the oxychloride,[230] it dissolves proteins under suitable conditions, but does not attack cellulose.

Much work still remains to be carried out on the character of plant tissues; it is probable that detailed investigations of the more important of these substances might lead to results having considerable technical significance.

R. Haller[231] regards the cuticle of the cotton fibre as a cellulose adsorption complex. Amylocellulose, the resistant portion of the starch granule, is thought to be a compound of silicic acid and amylose. According to G. Malfitano and M. Catoire,[232] its composition may probably be represented by the formula $[SiO_3(C_6H_{10}O_5)_n]H_2$, and the presence of combined silica may account for its marked resistance to hydrolysis.

Cellulose Ethers, Esters, etc.

Papers dealing with the chemistry of the cellulose ethers are comparatively few in number; very little progress appears to have been made in this branch of the subject, although the commercial preparation and utilisation of these products appear to be attracting a deal of attention.

In continuing their earlier work on the acetolysis of ethylated cellulose,[233] K. Hess and W. Wittelsbach[234] obtain as a final product of the reaction, a tetra-ethylbiose anhydride. They have made investigations of the molecular condition of this substance in solution, in various solvents.

According to M. Gomberg and C. C. Buchler,[235] all types of carbohydrates, including cellulose, which have been previously hydrated by suitable treatment with alkali, may be benzylated with benzyl chloride. Mono-, tri-, and tetra-benzyl derivatives appear to have been isolated, and are characterised by their resistance to the solvent action of cuprammonium solution. A new method of determining methoxyl values, which may be applicable to the examination of methylated celluloses, has been proposed by W. M. Cumming.[236]

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[228] *J.*, 1922, 94T.

[229] *J. Amer. Chem. Soc.*, 1922, **44**, 1668; *J.*, 1922, 752A.

[230] *Ann. Repts.*, 1921, **6**, 138.

[231] *Text. Forsch.*, 1921, **3**, 20; *J.*, 1921, 841A.

[232] *Comptes rend.*, 1922, **174**, 1128; *J.*, 1922, 429A.

[233] *Ann. Repts.*, 1921, **6**, 133.

[234] *Ber.*, 1921, **54**, 3232; *J.*, 1922, 94A.

[235] *J. Amer. Chem. Soc.*, 1921, **43**, 1904; *J.*, 1922, 71A.

The patent literature connected with the subject contains numerous details for the preparation and employment of cellulose ethers. H. Plauson[237] proposes to employ his colloid mill in their production.

An extensive study of the preparation of cellulose acetates from pine wood, sulphite pulp, and paper, has been made by E. Hägglund, N. Löfman and E. Färber,[238] who have investigated the conditions affecting the rate of acetylation of these materials, with the object of determining rapid methods of production. The use of hydrazine and hydroxylamine as accelerators in the acetylation of cellulosic materials has been dealt with.[239]

Important communications on the gelation of cellulose acetates have been made by E. Knoevenagel[240] in the course of an admirable and extremely exhaustive study of the subject. It has been noted that cellulose acetates which do not swell in water or alcohol, swell very considerably, with modification of their physical properties, in a mixture of these liquids. The swollen material may be readily saponified by treatment with 0·5*N* potassium hydroxide solution at room temperature, an accurate method of acetyl determination being based on this observation. The effect of various organic liquids and binary mixtures has been carefully studied with special reference to the physical conditions obtaining, and the degree and character of swelling consequent on treatment with these substances. Swelling is regarded as a phenomenon of a chemical nature. Experiments very similar to those made by R. O. Herzog and F. Beck,[241] on the solvent action of neutral salt solutions on cellulose and its derivatives, have been recorded by K. Schweiger,[242] who has dealt with the solubility of cellulose esters, and the lower products of cellulose acetolysis, in a number of neutral salt solutions.

Like P. P. von Weimarn[243] and the above-mentioned investigators, he finds that a relation exists between solvent power and the hydration of the ions of the respective salts.

The use of ethyl acetate, alone, or in admixture with ethyl alcohol, as a solvent for cellulose acetates and nitrates, has been investigated by H. F. Wilkie,[244] who has examined the viscosities and other physical characters of the solutions obtained.

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[236] *J.*, 1922, 20T.
[237] E. P. 183,908 ; *J.*, 1922, 748A.
[238] *Cellulosechem*, 1922, **3**, 13 ; *J.*, 1922, 247A.
[239] *L'Ind. Text.*, 1922, **38**, 181.
[240] *Koll.-Chem. Beihefte*, 1921, **13**, 194 ; 1922, **16**, 180 ; *J.*, 1921, 382A.
[241] *Ann. Repts.*, 1921, **6**, 127.
[242] *Z. physiol. Chem.*, 1921, **117**, 61 ; *J.*, 1922, 323A.
[243] *Ann. Repts.*, 1921, **6**, 126.

O. Torii,[245] in a review of the various methods proposed for the technical analysis of cellulose acetates, states that the Eberstadt process appears to be the most satisfactory one: he gives details of a modification thereof.

Cellulose acetates prepared by treatments involving the use of sulphuric acid or its derivatives, as catalysts, may contain free sulphuric acid, due to decomposition of sulpho-acetates invariably present. M. Entat and E. Vulquin[246] propose to estimate this acidity by means of a suitable process of electrometric titration.

Investigations of the viscosity of cellulose acetate solutions have been made by G. Barr and L. L. Bircumshaw,[247] presumably in connexion with work on the preparation of aeroplane dope. Determinations of the viscosity and density of 5% solutions of cellulose acetate in acetone and acetone-binary mixtures were made, the precise effect of the concentration of the second solvent on the viscosity of the solution being investigated.

The same subject has been dealt with by A. von Fischer,[248] who records examinations of the viscosity of cellulose esters in various solvents. The work was undertaken with the object of devising physical methods of control for the technical application of these compounds, and is therefore of considerable interest. It has been noted that cellulose acetates which yield good products show a minimum viscosity in acetone-alcohol solution when the solvent contains 80% by volume of acetone, and that nitrocelluloses giving good celluloid, have their viscosity in alcoholic solution lowered by increasing amounts of camphor.

B. Rassow[249] reviews the properties of cellulose formates, making observations on the formic acid content of these esters, the molecular ratios involved in their compositions, and their solubility in various solvents. Cellulose formates are stated to be very unstable substances.

A process for the preparation of cellulose butyrate has been patented by A. D. Little.[250] In the course of investigations on the production and alcoholysis of cellulose esters, A. Grün and F. Wittka[251] have prepared the cellulose esters of stearic and lauric acids, by treatment of the material with the corresponding acid chlorides in presence of pyridine. The mono-esters, which resemble the parent substance in general appearance, may be distinguished by their solubility in certain solvents and their behaviour towards fat-soluble dyes. Cellulose esters, as in the case of ethers, can be produced by treating cellulose in a highly dispersed state with the necessary reacting substances, with or without condensing agents. In this way, in addition to the usual organic esters of cellulose, the phosphate and sulphide of this compound may be prepared. This method of manufacture has been protected by H. Plauson,[252] who employs his colloid mill for the purpose of obtaining the necessary dispersion of cellulose.

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[244] *Chem. and Met. Eng.*, 1921, **25**, 1186.

[245] *Kogyo-Kwagaku Zasshi*, 1922, **25**, 118; *J.*, 1922, 367A.

[246] *Ann. Chim. Analyt.*, 1922, **4**, 131; *J.*, 1922, 541A.

[247] *Trans. Faraday Soc.*, 1921, **16**, *Appendix*, 72. *Physics and Chem. of Colloids*, *Dept. Sci. Ind. Res. Rpt.*, 1921.

[248] *Kolloid Zeits.*, 1921, **29**, 260.

[249] *Chem.-Zeit.*, 1922, **46**, 886.

[250] E. P. 167,143 *and* 182,820; *J.*, 1922, 748A, 894A.

[251] *Z. angew. Chem.*, 1921, **34**, 645; *J.*, 1922, 84A.

Little appears to have been published concerning the preparation or utilisation of the nitric esters of cellulose.

The use of these substances as emulsifying agents, as a means for the production of membranes for physico-chemical work, and the factors affecting their gelation, have been dealt with by H. N. Holmes and D. H. Cameron,[253] J. M. Looney[254] and J. Desmaroux,[255] respectively, the former investigators having employed their solutions in the production of chromatic emulsions.[256]

In the course of a discussion on "Colloids," held jointly by the Faraday Society and the Physical Society of London during the latter part of 1921,[257] interesting remarks were made by R. Robertson, who dealt with the more recent work on the viscosity of nitrocellulose solutions and its technical significance, and F. Sproxton, who reviewed the general field of the colloid properties of nitrocelluloses.

A detailed general account of the production and employment of these compounds in the manufacture of pyroxylin plastics has been published by J. R. Du Pont.[258] They form the basis of a new "plastic wood" composition introduced by the "Necol" Company.[259]

Investigations made by L. N. G. Filon and H. T. Jessop,[260] on the variation of the optical properties of celluloid with applied stress, throw considerable light on its behaviour during loading, and the results, expressed mathematically, are explained by supposing celluloid to consist of a fine-grained elastic skeleton and a plastic magma.

[252] E. P. 183,908 ; *J.*, 1922, 748A.

[253] *J. Amer. Chem. Soc.*, 1922, **44**, 66 ; *J.*, 1922, 239A.

[254] *J. Biol. Chem.*, 1922, **50**, 1 ; *J.*, 1922, 271A.

[255] *Mém. Poudres*, 1921, **18**, 169 ; *J.*, 1922, 388A.

[256] *J. Amer. Chem. Soc.*, 1922, **44**, 71 ; *J.*, 1922, 239A.

[257] *Physics and Chem. of Colloids, Dept. of Sci. Ind. Res. Rpt.*, 1921.

[258] *Chem. and Met. Eng.*, 1922, **26**, 11 ; *J.*, 1922, 137A.

[259] *Engineering*, 1921, **112**, 785.

[260] *Phil. Trans.*, 1922, **A223**, 89.

Experiments made by E. O. Holmes, jun., and W. A. Patrick [261] *on the effect of ultra-violet light on gels* tend to show that celluloid is decomposed by exposure to this agent.

Patents dealing with the production of cellulose esters, their conversion to plastics (involving the use of a variety of solvents and softening agents), and their employment in other connexions, have appeared, the majority presenting no strikingly novel features.

A non-inflammable nitrocellulose composition suitable for use as a binding material for driving belts or as a floor-covering, is obtained by dissolving nitrocellulose in the liquid non-volatile esters of phosphoric or thiophosphoric acids or their halogen substitution products, and adding suitable filling materials.[262] Cyclobutanone[263] and chlorophyll acetate[264] are among the solvents claimed for use with cellulose esters.

It is probable that only a fraction of the number of plastifying agents proposed will find actual technical application.

WOOD.

Communications dealing with the structural characteristics of lignified tissues are few in number, and no very great amount of attention appears to have been devoted to the subject of their microchemical detection. On the other hand, however, numerous papers dealing with the chemistry of the lignins have appeared. Much excellent work on these substances is being carried out in the various Continental laboratories.

In connexion with the subject of colour reactions for lignified material, reference may again be made to L. Rosenthaler and F. Kolles' extension of earlier work on the Prussian blue test,[265] and to C. van Zijp's observations on the use of benzidine hydrochloride as a staining reagent.[266] O. Adler[267] ascribes the intense green colour developed on heating small pieces of wood with a concentrated solution of phenylhydrazine hydrochloride in glacial acetic acid, to traces of anethole derivatives present in the wood.

P. Klason,[268] in dealing with the characters of the lignins (and their derivatives) of various coniferous trees, discusses the probable constitution of the *a*-substance, and proposes a formula for it.

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[261] *J. Phys. Chem.*, 1922, **26**, 25 ; *J.*, 1922, 323A.

[262] E. P. 156,096 ; *J.*, 1922, 542A.

[263] E. P. 184,671 ; *J.*, 1922, 807A.

[264] U. S. P. 1,397,986 ; *J.*, 1922, 53A.

[265] *Ber. deuts. pharm. Ges.*, 1921, **21**, 446.

[266] *Pharm. Weekblad*, 1921, **58**, 1539.

[267] *Biochem. Zeits.*, 1922, **128**, 32 ; *J.*, 1922, 346A.

[268] *Svensk Kem. Tidskr.*, 1922, **34**, 4 ; *Ber.*, 1922, **55**, 448 *et seq.* ; *J.*, 1922, 627A, 247A.

The methylation of lignin and its derivatives has been investigated by E. Heuser and his co-workers.[269] By repeated methylation of material isolated by the Willstätter-Zechmeister process, and of lignosulphonic acid, the methoxyl contents of these substances were considerably increased. It was hoped that oxidation of the methyl ethers would yield aromatic oxidation products, but an examination of the products of degradational oxidation gave negative results.

R. Willstätter does not accept the theory that lignin possesses an "aromatic" structure, but regards it as having a constitution of a carbohydrate character. His work, in collaboration with L. Kalb and G. von Miller,[270] on comparative reductions of pine lignin and various carbohydrates, tends to substantiate this view.

In continuation of work on the characters of straw lignin,[271] F. Pashke[272] gives details of the preparation of a number of its derivatives. By treatment of straw lignin with sulphuryl chloride under suitable conditions, and with phosphorus pentachloride, chlorinated derivatives may be obtained which might be utilised in the technical production of lacquers.

The ligninoid resins and tannins of spruce needles have formed the subject of an exhaustive examination by A. C. von Euler.[273]

Chemical and other investigations of the woods of Swedish pines and spruces, and of eucalyptus and the western white pine, have been made by H. E. Wahlberg,[274] and by S. A. Mahood and D. E. Cable,[275] respectively. The relative merits and demerits of the various processes available for the removal of resin from wood prior to cellulose manufacture, have been discussed at some length by H. Wenzl.[276]

A modification of the Cross and Bevan method of determining the cellulose content of wood, is described by E. Heuser and H. Casseus,[277] who employ a solution of chlorine in carbon tetrachloride as a chlorinating agent. The process is stated to be simple in operation, to give extremely concordant results, and to possess several advantages over the older method. The technical utilisation of chlorine as an agent for the separation of cellulose from wood has been dealt with by A. Cerruti[278] and by U. Pomilio,[279] the former writer discussing previous observations of the latter, who now compares the De Vains with the Cataldi process.

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[269] *Cellulosechem.*, 1921, **2**, 81 ; 1922, **3**. 78 ; *J.*, 1922, 665A.

[270] *Ber.*, 1922, **55**, 2637 ; *J.*, 1922, 893A.

[271] *Ann. Repts.*, 1922, **6**, 143.

[272] *Cellulosechem.*, 1922, **3**, 19 ; *J.*, 1922, 247A.

[273] *Ibid.*, 1921, **2**, 128 ; 1922, **3**, 1 ; *J.*, 1922, 171A.

[274] *Papierfabr.*, 1922, **20**, 1097, 1183, 1178 ; *J.*, 1922, 805A.

[275] *J. Ind. Eng. Chem.*, 1922, **14**, 933 ; *J.*, 1912, 934A.

[276] *Zellstoff u. Papier*, 1922, **2**, 228 ; *J.*, 1922, 935A.

[277] *Papierfabr.*, 1922, **20** (*Fest. u. Aus.*), 80 ; *J.*, 1922, 540A.

[278] *Giorn. Chim. Ind. Applic.*, 1922, **4**, 65 ; *J.*, 1922, 366A.

[279] *Chim. et Ind.*, 1922, **8**, 41 ; *J.*, 1922, 704A.

R. Hasenöhrl and J. Zellner,[280] in the course of an examination of the constituents of fungi, have been unable to isolate any specific cellulose-splitting enzymes from fungi attacking cellulosic materials, or to induce zymolysis of oak wood or soda-cellulose by treating these materials with extracts of fungal mycelia, or sporangia. Investigations of the effect of a species of *Polyporus* on oak, showed that development took place mainly at the expense of the soluble cell contents, the cellulosic constituents being comparatively immune to attack. It is thought that the actual decomposition of cellulose in wood may be brought about by bacteria living in symbiotic relationship with the fungus. H. Schmitz[281] has identified a number of enzymes present in species of *Polyporus* and *Fomes*.

Numerous papers dealing with the chemistry of xylan and xylose have appeared. A modification of the well-known phenylhydrazine method for the estimation of pentosans has been proposed by A. R. Ling and D. R. Nanji.[282]

T. Tadokoro[283] describes the characters of the absorption spectra of the phloroglucides of methyl- and hydroxymethylfuraldehyde.

Experiments on the hydrolysis of crude wood cellulose are recorded by G. Meunier.[284]

The utilisation of waste ligneous material is a matter of some importance; the remarks of C. S. Miner, J. P. Trickey, and H. J. Brownlee[285] on the production and uses of furfuraldehyde will therefore be of interest.

Wood Pulp.

An examination of the mechanism of the sulphite process has been made by R. N. Miller and W. H. Swanson,[286] who give details of numerous experimental cooks and make recommendations concerning the control of sulphite digestion. Determinations of the lignin contents of pulps during treatment throw some light on the rate of the removal of lignin from the material. The effect of the physical condition and nature of the wood employed, on the quality and characteristics of sulphite pulp, is discussed by B. T. Larrabee.[287]

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[280] *Monatsh.*, 1922, **43**, 21.
[281] *J. Gen. Physiol.*, 1921, **3**, 795.
[282] *Biochem. J.*, 1921, **15**, 406.
[283] *J. Coll. Agric. Hokkaido Imp. Univ.*, 1921, **10**, 52.
[284] *Comptes rend.*, 1921, **174**, 468; *J.*, 1922, 212A.
[285] *Chem. and Met. Eng.*, 1922, **27**, 299, 362.
[286] *Paper*, 1922, Apr. 19, 96.
[287] *Ibid.*, 1921, Nov. 2, 15.

In continuation of his earlier observations on the subject,[288] R. Sieber[289] deals with the analytical examination of sulphite liquors, having previously investigated the occurrence of thiosulphates and polythionates in these reagents.[290] The presence of thiosulphates in sulphite liquors prepared by the use of gases obtained by the complete combustion of sulphur or pyrites, is ascribed to the reaction of traces of sublimed sulphur carried over in the gas stream, polythionates being formed by subsequent reaction of thiosulphates with excess of sulphur dioxide; thio-compounds of both types may, however, be formed by the action of volatile arsenic and selenium derivatives. Methods for their estimation are proposed. A scheme for the analysis of reclaimed sulphite acid is suggested by G. P. Genberg.[291] W. T. Smith and R. B. Parkhurst[292] have examined the solubility of sulphur dioxide in suspensions of calcium and magnesium hydroxides. According to M. Neilson,[293] jack pine sulphite pulp, suitable for use in newsprint paper manufacture, can be obtained by an acid digestion, details of which are given. E. Sutermeister[294] deals with the pulping of decayed and stained wood.

The reddening of sulphite pulp is attributed to the presence of chromogenic lignin degradation products, which may be chemically fixed on the cellulose, or retained after the manner of dyestuffs. E. Heuser and S. Samuelson[295] find that whereas these objectionable impurities require a comparatively severe bleaching treatment for their complete removal, they may be destroyed by weak acid solutions of potassium persulphate.

R. J. Blair and E. Parke-Cameron[296] state that mechanical wood pulp may be stored in clean water for a considerable period of time without appreciable deterioration. Cold storage is found to be even more effective.

The sulphate process does not appear to have received a very considerable amount of attention though pulping trials of several new materials have been recorded and methods for the deodorisation of gases evolved during sulphate treatment have been discussed and patented. In this latter connexion, attention may be directed to the remarks of B. N. Segerfelt,[297] G. F. Enderlein,[298] and C. G. Schwalbe.[299]

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[288] *Ann. Repts.*, 1921, **6**, 146.

[289] *Zellstoff u. Papier*, 1922, **2**, 199; *J.*, 1922, 893A.

[290] *Ibid.*, 1922, **2**, 51, 106; *J.*, 1922, 499A.

[291] *J. Amer. Chem. Soc.*, 1922, **44**, 1918; *J.*, 1922, 896A.

[292] *Paper*, 1922, Apr. 19, 122; *J.*, 1922, 584A.

[293] *Pulp and Paper Mag.*, 1922, **20**, 61; *J.*, 1922, 247A.

[294] *Ibid.*, 1922, **20**, 513; *J.*, 1922, 584A.

[295] *Papierfabr.*, 1922, **20**, 1249, 1285, 1321; *J.*, 1922, 893A.

[296] *Pulp and Paper Mag.*, 1922, **20**, 64; *J.*, 1922, 247A.

[297] *Ibid.*, 1921, **19**, 1281; *J.*, 1922, 138A.

[298] *Paper*, 1921, Nov. 23, 9; *J.*, 1922, 95A.

[299] *Zellstoff u. Papier*, 1922, **2**, 175; *J.*, 1922, 746A.

E. Heuser and J. Haugeröd,[300] in the course of an investigation of the chemical characters and pulping qualities of *Typha domingensis*, a South American swamp rush, have determined the best conditions for digestion, whereby a pulp suitable, after bleaching, for the manufacture of cream or yellowish papers of medium quality may be obtained. According to G. J. Fowler and B. Bannerjee,[301] sugar cane refuse (*megasse*) may be converted into pulp suitable for wrapping papers, boards, etc., after preliminary treatment to remove sugars and non-cellulosic materials present.

Methods for the chemical determination of the degree of digestion of pulps, and the quantitative expression of their bleaching qualities, are of interest. R. Sieber, who has previously proposed measurement of the digestion of pulps by determination of the amount of chlorine absorbed by samples from a standard solution of bleaching powder,[302] finds the results obtained by this test to be influenced by the temperature and alkalinity of the bleaching liquor, necessitating modification of the method of procedure.[303]

In a subsequent communication he has examined the chlorine consumption values of sulphite pulps, estimated by this method, and the percentage of lignin present as determined by the Willstätter process.[304] The chlorine consumption value of a pulp is stated to be approximately proportional to the quantity of bleaching powder required for its treatment in bleaching. H. Roschier[305] proposes to make use of the reduction of potassium permanganate solution by pulps, under standard conditions, as a means for determining their degrees of digestion, while A. Tingle[306] suggests a method for obtaining the amount of bromine absorbed, this figure being convertible to a chlorine figure and serving as a measure of the bleaching qualities of pulps.

It is claimed that by bleaching pulp, first with a bleach liquor acidified by means of carbon dioxide to the extent of a two-thirds bleach, followed by final treatment with an ordinary alkaline bleach solution, under suitable conditions, a degree of whiteness superior to that produced by the usual process, and with a lower consumption of chlorine, may be obtained.[307]

Numerous papers dealing with the determination of resistant cellulose in pulps have appeared. The examination of pulps for viscose manufacture, with reference to discrepancies arising in carrying out α-cellulose determinations, has been dealt with by

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[300] *Papierfabr.*, 1922, **20**, 253 ; *J.*, 1922, 288A.

[301] *J. Indian Inst. Sci.*, 1921, **4**, 241 ; *J.*, 1922, 227A.

[302] *Ann. Repts.*, 1921, **6**, 146.

[303] *Zellstoff u. Papier*, 1921, **1**, 181 ; *J.*, 1922, 540A.

[304] *Ibid.*, 1922, **2**, 27 ; *J.*, 1922, 409A.

[305] *Ibid.*, 1922, **2**, 184 ; *J.*, 1922, 746A.

[306] *J. Ind. Eng. Chem.*, 1922, **14**, 40 ; *J.*, 1922, 137A.

[307] *Zellstoff u. Papier*, 1922, **2**, 6 ; *J.*, 1922, 408A.

P. Waentig,[308] who proposes a modification of the process.[309] C. G. Schwalbe and H. Wenzl,[310] employ a solution of barium hydroxide in examining the resistant cellulose content of pulps, and suggest a " baryta resistance " value in place of the α-cellulose value.

Comparative examinations of wood and cotton cellulose have been recorded by S. A. Mahood and D. E. Cable,[311] who make observations concerning the most suitable method of preparation for esterification purposes. L. E. Wise and W. C. Russell[312] regard cotton and wood cellulose as being constitutionally identical.

Waste Liquor.

Of the relatively few communications dealing with the characters and utilisation of sulphite-cellulose waste liquors, that of F. König[313] is one of the most interesting. Experiments are described in which the lignin present in these lyes was sulphonated by blowing the concentrated liquor into sulphuric acid, and the barium salt of lignosulphonic acid, prepared. The chemical and physico-chemical characters of this substance, which is stated to have the composition $C_{46}H_{40}O_{27}S_2Ba$, have been examined, observations being made on the properties of lignosulphonic acid, and on the nature of its oxidation. It is proposed to employ the barium salt in the preparation of the positive plates of secondary cells, the facts that it is readily ionised in solution and does not yield permanent products on oxidation being extremely advantageous. The aldehyde content of sulphite waste liquor spirit has formed the subject of an examination by E. Heuser, K. Schwarz and H. Magnus.[314] The first fractions in the rectification of the alcohol are stated to contain acetaldehyde to the extent of 10–11%, or even more. Reference is made to the occurrence of aldehyde in a free or polymerised form, and to the iodometric methods employed for its estimation.

Extensive observations on the combustion of sulphite waste liquors are recorded by E. Wirth,[315] who states that the average calorific value of the dry substance present, allowing for 10% of ash, may be taken as 4400 calories. He gives details for calculating the net calorific value of liquors for any concentration, and deals with the practical methods for the neutralisation of acidity and

[308] *Zellstoff u. Papier*, 1922, **2**, 12 ; *J.*, 1922, 408A.
[309] *Ibid.*, 1922, **2**, 225 ; *J.*, 1922, 935A.
[310] *Ibid.*, 1922, **2**, 75 ; *J.*, 1922, 409A.
[311] *J. Ind. Eng. Chem.*, 1922, **14**, 727 ; *J.*, 1922, 664A.
[312] *Ibid.*, 1922, **14**, 285 ; *J.*, 1922, 366A.
[313] *Cellulosechem.*, 1921, **2**, 93, 105, 117 ; *J.*, 1922, 9A.
[314] *Papierfabr.*, 1922, **20**, 1 ; *J.*, 1922, 190A.
[315] *Ibid.*, 1922, **20**, 65 ; *J.*, 1922, 171A.

concentration. By means of suitable plant it is possible to employ sulphite lyes for economical power production.

The patent literature contains the usual types of references to the evaporation and concentration of these effluents, to methods for utilising them in the production of fuels, adhesives, and textile finishing agents. R. J. Löffler[316] claims their use, in conjunction with proteins in the preparation of threads, films, and plastics, giving details of the manufacture of a patent leather varnish.

The addition of sulphite-cellulose waste liquors and the like to alkaline baths, to minimise degradation of animal fibres, has been referred to in an earlier section. A patent taken out by P. Goldberg, P. Onnertz, and A. Peters[317] in this connexion has been assigned to the Akt.-Ges. f. Anilin-Fabrikation, who have recently introduced a new protective agent under the name of "Protectol."

PAPER.

A method for the continuous digestion of rags is protected by V. Bernot and P. R. Fournier.[318] J. E. Aitken[319] recommends a fractional digestion process for the economical preparation of esparto pulp, giving details of the treatment. This process, patented by W. Raitt,[320] has been subjected to further modification.[321]

According to T. E. Blasweiler,[322] rye straw digested by the Steffen method is suitable for paper making.

C. Uhlemann[323] states that bulrushes and reeds are being utilised in Saxony for millboard manufacture; A. T. Masterman[324] patents a treatment of waste wattle bark and other tanyard refuse for this purpose. Among the various fibrous materials proposed for use in the making of paper and allied products, peat again appears.

E. W. L. Skark[325] deals with the significance of the various factors obtaining in the beating of pulp, and emphasises the need for a thorough control of the process. He reviews the methods proposed for measuring the degree of beating of pulps, discussing the results obtained during examinations of pulps prepared using various types of beating tackle, and describes a convenient type of instrument designed for the purpose.[326] It is known as a "stuff-spindle" and consists of a hydrometer-like appliance with an open stem and a gauze base of standard dimensions. On being placed in a cylinder of diluted pulp suspension, it sinks, due to the passage of water through the sieve-like base, the rate of sinking depending on the fineness of the pulp. Details of this instrument, and of a modified form, are given, along with an account of the methods of preparing the pulp suspensions and carrying out the test.

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[316] G.P. 346,832; *J.*, 1922, 665A.
[317] U.S.P. 1,419,497; *J.*, 1922, 548A.
[318] E.P. 178,962; *J.*, 1922, 542A.
[319] *Paper*, 1921, Nov. 2, 17; *J.*, 1922, 52A.
[320] E.P. 15,779, 16,488; *J.*, 1913, 785; 1916, 1009; 1921, 191R.
[321] E.P. 171,482; *J.*, 1922, 53A.
[322] *Papierfabr.*, 1922, **20**, 1025, 1061, 1101; *J.*, 1922, 746A.
[323] *Ibid.*, 1922, **20**, 962; *J.*, 1922, 665A.
[324] E.P. 182,884; *J.*, 1922, 665A.
[325] *Papierfabr.*, 1921, **19**, 509; *J.*, 1922, 9A.
[326] *Ibid.*, 1922, **20**, 845; *J.*, 1922, 583A.

In a later article,[327] he discusses the effect of the type of digestion treatment employed, on the colour and other characters of jute half-stuff prepared from bagging, special attention having been paid to the effect of the changes consequent on storage in the drainers, on the beating properties of the pulp. Half-stuff prepared by lime digestion does not appear to have its beating properties affected by storage, but on the other hand, prolonged storage of material, well digested with caustic soda, or with caustic soda and sodium sulphide, results in the half stuff working better in the beater, the maximum beneficial alteration being effected in from two to three weeks. It has been noted that storage of the fully-beaten pulps in the stuff chest, in presence of excess of water, also results in a "softening."

An exhaustive treatment of the colloid chemistry of rosin sizing is given by R. Sieber,[328] who deals with extensive experiments on the precipitating effect of metallic salts on various rosin sols, and with the fixation of the sizing ingredients by different pulps. The sizing process is stated to involve both chemical and electro-colloidal phenomena. T. E. Blasweiler[329] has contributed a series of articles on the use of sodium silicate in pulp sizing, giving details of the precautions to be observed in applying it along with rosin, and the various advantages to be gained from its use in conjunction with numerous sizing agents. G. Muth[330] claims the use of coumarone- and indene-resins in pulp sizing. Rubber latex, employed along with suitable coagulants, is stated to be an advantageous addition to the pulp during beating. It is claimed that it accelerates hydration, and that paper produced from the stock has improved strength. Its possible use has been reviewed by F. Kaye.[331]

W. C. Holmes[332] deals with the dyeing of stock in the hollander. Direct cotton dyestuffs are stated to be particularly suitable for the production of dark shades, if properly applied.

Communications and patents dealing with the actual manufacture, and with improvements in the production of paper, are few in number; on the other hand, new agents have been proposed for the coating of papers and for the waterproofing and stiffening of articles prepared therefrom.

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[327] *Papierfabr.*, 1922, **20**, 881, 917, 957 ; *J.*, 1922, 664A.

[328] *Zellstoff u. Papier*, 1921, **1**, 15 *seq.* ; 1922, **2**, 99, 134 ; *J.*, 1921, 842A ; 1922, 746A.

[329] *Papierfabr.*, 1921, **19** (*Fest.- u. Aus.*), 43, 625, 809, 875, 992, 1108, 1217, 1322, 1505, 1842 ; *J.*, 1922, 95A.

[330] G.P. 349,595 ; *J.*, 1922, 665A.

[331] *Indiarubber J.*, 1922, **64**, 435 ; *J.*, 1922, 806A.

[332] *J. Ind. Eng. Chem.*, 1922, **14**, 908 ; *J.*, 1922, 935A.

Among these are to be found preparations of humic acid obtained from peat,[333] condensation products of formaldehyde with urea or its derivatives,[334] and various proteic materials hardened by treatment with "methylolformamide."[335]

S. C. Bhatnagar[336] has investigated the waterproofing effect of various insoluble metallic soaps on articles of paper or paper pulp, and makes observations on the relative efficiencies of these reagents.

Bentonite, a highly colloidal clay, which has been proposed for use in various connexions in textile and paper technology, now finds further application as an agent for the removal of printing ink from waste paper.[337]

In connexion with the testing of papers, attention may be directed to a number of communications of interest.

The method proposed by H. F. Coward and G. M. Wigley[338] for the determination of acidity or alkalinity in cotton, might conceivably be applied in examinations of paper. H. Krull and B. Mandelkow[339] state that the phloroglucinol absorption process devised by Cross, Bevan, and Briggs for the estimation of mechanical wood pulp, is eminently suitable for the determination of mechanical pulp in "news," and similar printing papers, providing a modified form of calculation be adopted.

An ingenious device (termed the "piezo-micrometer") for determining the thickness of a sheet of paper submitted to a definite known pressure, is described by J. Strachan.[340] L. R. Ingersoll[341] gives details of his polarisation glarimeter, which enables the gloss of calendered papers to be accurately measured and standardised.

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[333] L. Ubbelohde, G.P. 303,324, 305,006-305,010, 307,098; *J.*, 1922, 704A.

[334] F. Pollak, E.P. 157,416; *J.*, 1922, 459A.

[335] A. Lutz, E.P. 156,514; *J.*, 1922, 367A.

[336] *J. Phys. Chem.*, 1922, **26**, 61; *J.*, 1922, 324A.

[337] H. R. Eyrich and J. A. Schreiber, U.S.P. 1,421,195; *J.*, 1922, 628A.

[338] *J. Text. Inst.*, 1922, **13**, 121T; *J.*, 1922, 497A.

[339] *Papierfabr.*, 1922, **20**, 1213; *J.*, 1922, 806A.

[340] *Proc. Tech. Sect. Papermakers' Assoc.*, 1922, **3**, 20; *J.*, 1922, 936A.

[341] *Paper*, 1921, **29**, Oct. 26.

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BLEACHING, DYEING, PRINTING, AND FINISHING.

By W. Harrison, M.Sc., F.I.C.

Introduction.

With regard to the application of science in the textile industry, R. S. Willows[1] discusses the place of the physicist and shows that most of the problems met with in the textile industry are physical rather than chemical. As a matter of fact a chemist without knowledge of physics would be of little value in the textile industry. The textile chemists are men who have made a special study of textile problems and to do this they have found it necessary to acquire knowledge of chemistry, physics, and mechanics, and sometimes higher mathematics.

Hitherto there has been no means of classifying these men who have not found it necessary to learn sufficient chemistry to qualify them as chemists or sufficient physics to qualify them as physicists; nevertheless, their value in industry is greater than that of the pure chemist or physicist. The Textile Institute has commenced a scheme for the granting of Fellowships and Associateships in Textile Technology. The qualifications for admission to Associateship include a general knowledge of textile processes such as is given in a three years' course at some of our technical colleges, and two years' actual experience in the textile industry. The Fellowship is intended for those men who, by direct personal effort, have advanced the progress of science in the textile industry, and one of the qualifications is that they shall have spent five years in the industry, that being regarded as the minimum period in which a man, whether scientifically trained or not, can acquire a good knowledge of textile technology. It is hoped by this scheme to pick out those men specially qualified to undertake textile research with some hopes of success.

Wool Scouring.

An interesting piece of work is described by A. M. King,[2] on the effect of salts on the viscosity of soap solutions. The addition of sodium chloride to a $N/2$ solution of sodium palmitate increases the viscosity, the effect continuing up to $N/2$ NaCl, but larger quantities of sodium chloride produce a decrease in viscosity. A similar effect was observed with potassium oleate and potassium chloride. It is interesting to compare these results with the observations of Shorter and Ellingworth[3] on the drop number of soap solutions.

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[1] *J. Text. Inst.*, 1921, **12**, 465.

[2] *J.*, 1922, 147T.

In the scouring of wool with soap solutions it has been proved by analytical methods, in a communication from the British Research Association for the Woollen and Worsted Industries,[4] that the wool removes more of the alkali than of the fat, hence the scouring liquor tends to accumulate free fatty acid. This has been known for a long time by practical men, who have overcome the effect by adding sodium carbonate. Free caustic soda is much more effective when used in suitable quantities, and has been successfully tried on the large scale by the writer. The absence of chemists in works where scouring of wool is carried out renders such a method of little commercial value. The results of the above-mentioned investigations point to the conclusion that the method used by the practical men, whatever its origin, is on the whole, scientifically sound.

The paper cited appears to depart from the custom of scientific organisations, in so far that the authors' names are not given. In earlier communications from this Research Association, the authors' names appeared in the customary manner. Is is pleasing to know that the other Research Associations are following the custom.

J. Schofield[5] gives some practical points on the scouring of wool, particularly that containing free fatty acid, presumably added in the processes of preparing and spinning.

The process of scouring such wool is termed the saponification scour by the author. Other scouring processes are also dealt with.

A process of degreasing wool by means of trichloro-ethylene forms the subject of a patent by T. A. Coghlan.[6]

COTTON BLEACHING.

The effect of scouring and bleaching on the strength of cotton fabrics forms the subject of a paper by J. Huebner.[7] The results apply to the fabric on which the work was done, as the effects are necessarily dependent on the nature and construction of the fabrics, as well as of the yarns from which they are made.

The bleaching of cotton by means of hypochlorites at elevated temperatures, has been found by P. Heermann and H. Frederking[8] to produce pronounced tendering. On the other hand M. Freiberger[9] contends that with strengths up to 1 gram of chlorine per litre, bleach liquors may be heated to 40° C. with perfect safety. At the shorter time necessary to complete the bleaching under these conditions, the amount of oxycellulose produced is said to be less than in the longer cold-process.

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[3] *Proc. Roy. Soc.*, 1916, **A92**, 232.

[4] *J. Text. Inst.*, 1922, **13**, 127 ; *J.*, 1922, 626A.

[5] *J. Soc. Dyers and Col.*, 1922, **38**, 76.

[6] E.P. 170,645 ; *J.*, 1921, 885A.

[7] *J. Soc. Dyers and Col.*, 1922, **38**, 29 ; *J.*, 1922, 213A.

[8] *Textilber.*, 1922, **3**, 61 ; *J.*, 1922, 214A.

R. L. Taylor[10] discusses the comparative bleaching action of chlorine and hypochlorous acid. Processes of bleaching cotton by means of peroxides are described by W. Francke,[11] and by L. Kollmann.[12] A summary of recent innovations in bleaching is given by Oelker.[13]

E. Ristenpart[14] described investigations on a new process of bleaching patented by Zellstoff-fabrik Waldhof, in which cotton is subjected to the action of acid bleaching solutions, followed by alkaline bleaching liquors. The results are said to be superior to those obtained by using the alkaline liquors first. Solutions containing 1 gram of chlorine per litre give by this method a whiteness equal to that obtained with 4 grams of chlorine per litre in the ordinary manner, the strength of the fabrics being greater by the new method.

MERCERISING.

H. Lowe, the inventor of the present-day process of mercerising under tension, points out in a recent paper[15] the importance of adequate twist and an equal distribution of fibres throughout yarns for mercerising. He shows that the actual diameter of a mercerised thread is, in general, less than that of the same yarn before mercerising, the effect being due to the compression produced on the inner layers by the tendency towards straightening of the fibres during the period under tension. The effect of mercerising on the dyeing properties of cotton has been discussed by J. Pokorny,[16] who says that basic properties are imparted, the effect being greater if Koechlin's alkaline chrome mordant is used with sufficient alkali to cause mercerisation.

Numerous experiments have recently been made by T. Barratt and J. W. Lewis[17] on the heat developed by the action of caustic soda on cotton. They find that the amount of heat developed increases with the concentration of the caustic soda used. The curve showing the heat produced with different concentrations of caustic soda is similar in character to curves obtained by previous authors for the absorption of caustic soda at different concentrations. No explanation of the heat development is put forward. R. S. Willows, T. Barratt, and F. H. Parker[18] describe some interesting experiments on the mercerisation of single cotton fibres. They find that under a given tension of 50 mg. per single fibre, cotton begins to shrink when the caustic soda lies between 20° and 25° Tw. (sp. gr. 1·1—1·125), the maximum shrinkage being attained at about 30° Tw. (sp. gr. 1·15). At a temperature of 0° C. the maximum is attained at a lower concentration, 25° Tw.

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[9] *Textilber.*, 1921, **2**, 428.

[10] *J. Soc. Dyers and Col.*, 1922, **38**, 93 ; *J.*, 1922, 368A.

[11] *Textilber.*, 1922, **3**, 108 ; *J.*, 1922, 808A.

[12] *Mitt. Forschungsinst. Text. Ind. Wien*, 1921, **1**, 16; *J. Text. Inst.*, **1922**, **13**, 103A.

[13] *Deuts. Faserst.*, 1922, **4**, 27 ; *J. Text Inst.*, 1922, **13**, 127A.

[14] *Textilber.*, 1922, **3**, 363 ; *J.*, 1922, 666A.

[15] *J. Soc. Dyers and Col.*, 1922, **38**, 296 ; *J.*, 1922, 54A.

[16] *Ibid.*, 1922, **38**, 248 ; *J.*, 1922, 894A.

[17] *J. Text. Inst. Trans.*, 1922, **13**, 113.

The effect of kier boiling, scouring, extraction with solvents, and of mercerisation under tension, is described. These experiments show quite clearly that untreated fibres shrink more than fibres which have been boiled or mercerised, and confirm the experiments of the writer[19] on the internal stresses in cotton fibres. It is likely from these last-mentioned experiments that the conditions of growth or ripeness of the cotton fibres will have a considerable influence on the amount of shrinkage. Barratt and Lewis were unable to find evidence of the different behaviour of the cuticle and internal parts of the fibre. They mention that ammoniacal copper solution has a greater dissolving action on cotton containing caustic soda of mercerising strength than on cotton not containing this substance, although previously treated with it. This is well known, and has been made use of in industry for the production of cellulose solutions for artificial silk spinning.

R. S. Willows and A. C. Alexander[20] have made a series of experiments on the change in sectional area and in volume of cotton fibres on mercerising. They find two maxima, one at 25° Tw. and a higher one at about 45° Tw., at which stage the sectional area is increased by 280% and the volume by 260%. On washing the area becomes 210% and the volume 200% greater than in untreated fibres.

When short lengths of cotton fibres are treated with 30° Tw. caustic soda the inner parts of the fibres bulge out at the ends over the cuticle. The authors mention that the force required to move a substance like cotton along a narrow bore tube of the diameter of the cotton fibre must be enormous and the cuticle must be extraordinarily strong. It does not necessarily follow that the bulging is caused by great pressure of the cuticular layers on the interior; the freedom to swell of the cellulose at the cut ends of the fi[illegible] J. is quite sufficient to account for the result. It is clear

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[18] J. Text. Inst. Trans., 1922, 13, 229; J., 1923, 51A.

[19] Proc. Roy. Soc., 1918, A94, 460.

[20] J. Text. Inst. Trans., 1922, 13, 237; J., 1923, 52A.

however, that the inner parts have greater swelling power than the external layer, which is most probably composed of cellulose of more compact form; this is a very important observation. A similar condition was found by the writer[21] to exist with starch granules.

The bulging was found by Willows and Alexander to be most pronounced between 30° and 40° Tw., but not very distinct above 45° Tw., although at this stage the maximum increase in sectional area was observed. The reason suggested is that the cuticle becomes more extensible at the higher concentrations of caustic soda, thus diminishing the difference in swelling power of the internal and external layers.

It is stated that fibres which have been tendered in any way, do not show this bulging of the inner parts over the ends of the cuticular layer.

The two papers above mentioned form a valuable addition to the literature on mercerisation. To find a full scientific explanation of mercerisation will require very much more work of this kind. A few interesting conclusions may be drawn by correlating the two papers. In the first paper the maximum shrinkage was noticed at 30° Tw., while in the second paper the maximum increase in sectional area was found at 45° Tw., but at this stage no bulging of the inner substance over the outer layers was observed. This bulging was, however, found to be greatest between 30° and 40° Tw., that is to say, roughly about the same concentration as produced maximum shrinkage. As the shrinkage takes place against a load it may be regarded as a tension. Thus the maximum tension is produced when the cuticle offers greatest resistance to the swelling forces.

The writer has attempted on several occasions to calculate the theoretical tension produced by internal forces acting at right angles to the inner surface of a hollow tube. Such a calculation cannot, however, be made without making assumptions regarding the physical properties of the substance of the tube, and in the case of cotton there are no means of measuring these properties, which appear to vary considerably. In the case of most substances these forces would tend to increase the diameter and shorten the length of the tube.

The tension required to bring back the cotton fibres to their original diameter must increase with increase in the area of the swollen colloid; hence it would be found that this tension would be a maximum at about 45° Tw., which is the concentration most useful for mercerising cotton yarns and fabrics. The question of internal stresses in cotton fibres is strongly brought to the front by the two papers referred to.

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[21] *J. Soc. Dyers and Col.*, 1916, 32, 32.

W. Marshall[22] describes experiments on the mercerisation of ramie and finds that an improvement in lustre is produced, as well as an increase in strength. Ramie has been mercerised on previous occasions, and samples were shown at an Exhibition arranged by the Textile Institute in 1920. The amount of ramie used for textiles in this country is not sufficient to promise any immediate commercial development in ramie lustred by mercerisation or by other means.

COTTON DYEING.

New mordants for the dyeing of basic colours on cotton are described by F. Bayer u. Co.[23] These consist of phenolic derivatives containing sulphur, one example being the product obtained by boiling phenol with caustic soda and sulphur.

H. Wagner[24] states that katanol is a sulphur-containing mordant for basic colours, while tamal (a formaldehyde compound of a naphthalenesulphonic acid) has also been found useful for this purpose.

In the dyeing of direct cotton colours R. Auerbach[25] finds an optimum concentration of salt for increasing the dyeing with direct colours. The same observation was made in 1912 by the writer,[26] who also found that by the addition of protective colloids this optimum concentration was raised considerably.

R. Haller and H. Russina[27] made experiments on the dialysis of direct cotton colours, with and without the addition of salts. They found that in presence of salt more dye passed through the dialyser than in its absence. From this observation they conclude that salt plays the part of a protective colloid. The authors are evidently unfamiliar with Bayliss's work on Congo Red, or with Donnan's theory of membrane equilibria. The effects described by Haller and Russina are most probably due to the electrical action of the dialysing membrane.

In this connexion H. Masters[28] finds that when purified cotton is extracted with a neutral salt solution the extract is acid. This observation was first made in 1912 by the writer,[28] who applied it in the explanation of the dyeing of cotton with direct cotton and other colours.

M. Battegay and J. Claudin[29] bring forward experimental evidence in support of the idea that in vat dyeing, in addition to the simple deposition of the dye in the interstices of the fibre, there exist other forces either chemical or adsorptive.

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[22] *J. Soc. Dyers and Col.*, 1922, **38**, 293 ; *J.*, 1923, 52A.

[23] E.P. 173,313 ; *J.*, 1922, 139A.

[24] *Farben-Zeit.*, 1922, **27**, 3015 ; *J.*, 1922, 705A.

[25] *Koll.-Zeits.*, 1922, **30**, 166; *J.*, 1922, 324A.

[26] *J. Soc. Dyers and Col.*, 1918, **34**, 138.

[27] *Koll.-Zeits.*, 1922, **30**, 249 ; *J.*, 1922, 460A.

[28] *Chem. Soc. Trans.*, 1922, **121**, 2026 ; *J.*, 1922, 977A.

[29] *Chim. et Ind.*, 1921, **6**, 592.

J. Pokorny[30] gives some interesting notes on the dyeing properties of cotton mordanted with an alkaline chrome mordant. Two methods of preparing the mordant are given, the most economical being the following: 1000 g. of chrome alum is dissolved in 5 litres of hot water and cooled to 10° C. This is poured slowly and with rapid stirring into $2\frac{1}{2}$ litres of caustic soda of 72° Tw., cooled to 10° C. The alkaline mordant obtained has a specific gravity of about 1·16 (32° Tw.). Cotton is treated with this mordant, allowed to stand several hours, and washed with cold water.

Cotton mordanted in this way has an increased absorptive capacity for the ordinary mordants, for many acid colours such as Alizarine Saphirol, Eriochrome Azural, etc., for diazo and tetrazo derivatives of amines and for phenolic compounds, such as salicylic acid, chromotropic acid, etc.

For the production of effect threads in cotton dyeing, L. Cassella u. Co.[31] convert the cotton into benzoate by means of alkali and a solution of benzoyl chloride in benzene. The same result is obtained by partial conversion into cellulose acetate.[32]

Similar effects are said to be produced by the use of naphthalenesulphonic acids, benzidinesulphonic acids, and sulphonated vegetable oils by precipitating with a salt of tin.[33]

WOOL AND SILK DYEING.

Interesting notes on the dyeing of chrome mordanted wool are given by A. Ganswindt.[34] Apparently the best effects are obtained when the mordanting metal exists both in an oxidised and a reduced state.

Experiments on the mordanting of wool with chromium are described by A. B. Craven.[35] Advantages are said to be obtained by after-treating the mordanted wool with soda ash prior to dyeing.

A long and interesting account of the development of processes for dyeing wool in fast colours is given by B. Wuth.[36] Developments are described in the alizarin group, the gallocyanine series and the *o*-hydroxy- and *o* amino-azo dyestuffs, which have the property of combining with metallic substances. Mention is made of the Metachrome, Monochrome, Eriochrome, and Chromosol methods of dyeing. Recent work on the indigo, thioindigo, and indanthrene series is also mentioned.

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[30] *J. Soc. Dyers and Col.*, 1922, **38**, 248; *J.*, 1922, 894A.

[31] G.P. 346,883; *J.*, 1922, 249A.

[32] G.P. 347,130; *J.*, 1922, 249A.

[33] G.P. 340,454; *J. Soc. Dyers and Col.*, 1922, **38**, 21.

[34] *Textilber.*, 1922, **3**, 151; *J.*, 1922, 411A.

[35] *J. Soc. Dyers and Col.*, 1922, **38**, 108; *J.*, 1922, 368A.

[36] *Ibid.*, 1922, **38**, 241.

J. I. M. Jones[37] discusses the dyeing of the acid alizarin dyestuffs, and mentions many of the points given by Wuth. The names of the British dyestuffs corresponding to those hitherto made on the Continent are given.

J. Brandt[38] describes a process for dyeing azo colours on wool, in which the wool is first boiled in a solution of a naphthol, naphthylamine, or aminonaphthol and subsequently coupled with a diazotised amine.

A process of dyeing vat colours on wool is given by L. Kollmann.[39] Wool is dyed dark blue by three immersions in a vat containing 15 g. of 20% indigo paste, 5 g. of hydrosulphite, 5–15 g. of prepared chalk or the equivalent of zinc oxide, per litre at 75° C. In another method the wool, 10 parts, is dyed for ½–1 hour at 75°–100° C. with 3 parts of 20% indigo paste, 10 parts of hydrosulphite, and 15 parts of prepared chalk in 1000 parts of water. Hydron Blue is dyed in a similar manner, but zinc oxide cannot be used.

For protecting wool and silk against the action of alkali in the dyeing of vat colours, sulphite-cellulose liquor is claimed by Akt.-Ges. f. Anilinfabrikation.[40]

The use of Protectol, which is probably the same as the above, in the dyeing of wool and silk with vat colours, forms the subject of a paper by A. Edge.[41]

For the production of effect threads wool is treated with the soluble condensation products of phenols with aldehydes, the dyeing affinity being thereby reduced.[42]

F. Münz and R. Haynn[43] state that when wool is treated with acetic anhydride in the presence of a catalyst such as sulphuric acid its affinity for acid colours is destroyed. As an example, 1 kg. of wool is treated with 1 litre of acetic anhydride, 4 litres of acetic acid, 140 g. of sulphuric acid, and 77 g. of dimethylaniline for 1½ hrs. at 57°–58° C. The treated wool is then mordanted, if desired, with chromium acetate and formic acid.

DYEING OF CELLULOSE ACETATE SILK.

W. E. Sanderson[44] describes the various processes used for the dyeing of cellulose acetate silk, some of which were given in the last volume of these reports.

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[37] *J. Soc. Dyers and Col.*, 1922, **38**, 201.

[38] *Bull. Soc. Ind. Mulhouse*, 1921, **87**, 337 ; *J.*, 1922, 361A.

[39] *Textilber.*, 1921, **2**, 279 ; *J. Text. Inst.*, 1922, **13**, 16.

[40] E.P. 183,868 ; *J.*, 1922, 705A.

[41] *J. Soc. Dyers and Col.*, 1922, **38**, 136 ; *J.*, 1922, 497A.

[42] G.P. 347,197 ; *J.*, 1922, 249A.

[43] *Chem.-Zeit.*, 1922, **46**, 945 ; *J.*, 1922, 895A.

[44] *J. Soc. Dyers and Col.*, 1922, **38**, 162.

Mention is made of a new method of saponification, in which the cellulose acetate is soaked in a strong solution of common salt containing caustic soda.[45] The British Cellulose and Chemical Manufacturing Co. and L. G. Richardson[46] claim the use of borates, silicates, aluminates, or acetates as additions to the caustic soda used for saponification.

Sanderson shows that the effect of magnesium or zinc chloride patented by Clavel as an assistant for dyeing basic colours, is due to a salting-out effect, sodium chloride being quite as good, but cheaper. Several simple azo dyes are mentioned which have a distinct affinity for cellulose acetate, the affinity being increased by the addition of a neutral salt. The absorption of the free bases of dyestuffs, such as Spirit Blue, from suspension in water is mentioned. The production of a black by the oxidation of *p*-aminodiphenylamine is referred to, but no details are given.

The dyeing of cellulose acetate by the foam method forms the subject of a patent by A. Clavel.[47]

In a recent patent of W. Harrison and Burgess, Ledward and Co.,[48] processes are described for the dyeing of direct cotton colours, sulphide colours, vat colours, and basic colours on acetate silk. A direct colour such as Diamine Sky Blue, which has no affinity for cellulose acetate under ordinary conditions, was found to be absorbed almost completely from a dyebath when converted into a colloidal solution by means of a suitable precipitant, such as dianisidine in presence of a protective colloid. As would be expected from the chemically unstable character of such colloidal complexes, the colour is entirely removed by alkaline liquids. When, however, a similar method is applied to vat colours which, after absorption by the silk, are oxidised by the air and become converted into stable colloidal form, fast dyeings are readily produced.

R. Clavel[49] states that the dyeing of cellulose acetate is not, as hitherto generally supposed, merely a physical phenomenon of adsorption, but that dyeing is due to the presence in the dyestuff of chemically active groupings, which enable the dye to combine chemically with the cellulose acetate. The following groups are claimed as active groups: hydroxyl, amino, imino, imide, nitro, nitroso, isonitroso, acidylamino, and azo groups. Carbonyl groups are said to be indifferent but sulphonic groups weaken or arrest the power of chemical combination.

As examples of dyestuffs containing active groups the following are mentioned: Pyramidol Brown, with four hydroxyl groups; Chrome Violet and Alizarin, with two; Magenta, with three amino groups; Rhodamine, with one ethylamino and one diethylamino group; Gallocyanine, with one hydroxyl and one dimethylamino group; Indanthrene, with two imino groups, and Algol Rose, with one hydroxyl and one acidylamino group. If this theory were true the production of dyestuffs suitable for cellulose acetate dyeing would be a comparatively simple matter.

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[45] E.P. 150,980; *J.*, 1921, 692A.
[46] E.P. 175,486, 176,034; *J.*, 1922, 289A.
[47] E.P. 176,535; *J.*, 1921, 579A.
[48] E.P. 179,384; *J.*, 1922, 543A.
[49] E.P. 182,830; *J.*, 1922, 666A.

While within certain limits it is quite possible that the dyeing may be governed to some extent by these so-called active groupings, it is by no means certain that the dyeing of cellulose acetate is a chemical phenomenon. The writer considers that the process of dyeing this fibre is entirely a solution phenomenon. If Clavel's chemical theory were correct, the effect of these active groupings should always be the same, and the ordinary chemical activity of these groupings should be inhibited by their chemical combination with the cellulose acetate. Neither of these conditions holds in practice. For example, when comparing aminoazobenzene with its derivatives, containing hydroxyl or amino groups meta to the parent amino group, it is found that the aminoazobenzene is almost completely exhausted from the bath by cellulose acetate silk, the dye containing the hydroxyl group comes next, and the dye containing a second amino group is least exhausted. As the colouring power of these compounds is not the same, the absorption cannot be judged from the depth of colour produced in the silk. The experiment clearly shows that the addition of the so-called active groups, hydroxyl and amino, reduces the affinity of the parent aminoazobenzene for the silk. The effect is due to increased solubility in water.

In the case of simple amino compounds dyed on acetate silk the free amino group is readily diazotised, showing that the grouping cannot be chemically combined with the silk.

The observation of Sanderson that salts increase the absorption of both acid and basic colours is favourable to the opinion that the dyeing is a solution phenomenon, the salts merely reducing the solubility of the dyestuff in the water.

The strongest support to the solution theory is given by observations on the dyeing of cellulose acetate with colours produced in the fibre by reactions which take place in organic solvents, but not in water. This work is not yet published.

Of more recent developments A. G. Green and K. H. Saunders[50] describe a series of dyestuffs under the name Ionamines, which are absorbed by cellulose acetate. These dyes belong to the same type as the soluble azo dyes patented by the Society of Chemical Industry in Basle.[51] All these dyes contain substituted amino groups, in which the hydrogens are replaced by methyl and by sulphonic groups, respectively. Such dyestuffs are hydrolysed in dilute solution by acids with formation of the corresponding aminoazo compounds. The dyeing is then due to the aminoazo compounds. These ω-methylsulphonic acid derivatives have the advantage of greater solubility than the parent aminoazo compounds. Practically all simple aminoazo compounds are absorbed by cellulose acetate silk, but this does not apply to the corresponding ω-methylsulphonic acids, some of which have no affinity whatever for the silk. A few dyes of this type were made and used by the writer independently of Green and Saunders, but as they were absorbed less readily than the corresponding aminoazo compounds the work was not continued. Green and Saunders have, however, made a large number of these compounds, from which they have made a selection for bulk manufacture, under the names Ionamine A, B, G, GA, H and L. By using these dyes in conjunction with ordinary direct cotton colours, both cotton and acetate silk can be dyed in one bath either the same or different colours.

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[50] *J. Soc. Dyers and Col.*, 1923, **39**, 10; *J.*, 1923, 138A.

[51] E.P. 172,056-7; *J.*, 1922, 51A.

PRINTING.

Special effects are produced in printing by crumpling fabrics into an irregular perforated cylinder which is then closed and immersed in a dye bath. Irregular markings are produced by the penetration of the dye through the holes in the cylinder. Multicoloured effects are obtained by repeating the operation with other dyes.[52]

R. S. Willows, F. T. Pollitt, and T. Leach[53] produce effects by embossing with hot rollers fabrics containing 7–15% of moisture, and then dyeing, mercerising, or parchmentising the embossed fabrics. The novelty apparently lies in the combination of the two treatments, as the amount of moisture specified is within the range used in practice for the ordinary embossing process.

R. Haller and F. Kurzweil[54] give quantitative figures for the amount of alumina, lime, Alizarin, and Turkey-red oil fixed during steaming of a fabric printed with a paste of given composition.

H. Sunder[55] claims an improvement in the chlorate-prussiate discharge process of printing by the use of boric acid in place of the greater part of the citric acid usually used.

J. Pokorny[56] states that Leucotrope O is a valuable assistant for the discharge printing of basic colours on a tannin-antimony mordant by means of Hydrosulphite NF.

C. Sunder[57] makes use of sodium tungstate for the fixation of basic colours by printing of reserve pastes under Aniline Black.

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[52] Calico Printers' Assoc., F. O. Ashmore, and F. Cochrane, E.P. 172,193; *J.*, 1922, 55A.

[53] E.P. 171,802; *J.*, 1922, 55A.

[54] *Textilber.*, 1922, **3**, 21; *J.*, 1922, 139A.

[55] *Bull. Soc. Ind. Mulhouse*, 1921, **87**, 343; *J.*, 1922, 139A.

[56] *Ibid.*, 1921, **87**, 572; *J.*, 1922, 290A.

[57] *Ibid.*, 1922, **88**, 78; *J.*, 1922, 461A.

Marbled effects are produced by the use of dyestuffs insoluble in water, but soluble in an oil, which are dissolved or emulsified in oil, and applied to the surface of water. Different colours are intermingled by drawing a comb over the surface of the water. The textiles are brought into contact with the coloured surface and absorb the colours therefrom.[58]

FINISHING AND PROOFING.

W. P. Dreaper[59] claims the use of metallic tungstates for fireproofing of artificial silk filaments before conversion into staple fibre. Transparent effects are produced on cotton by treatment with sulphuric acid of sp. gr. 1·515–1·536, washing, and drying under great tension, repeating the operation with stronger acid (sp. gr. 1·565–1·597) and finally mercerising.[60]

Bayer u. Co.[61] waterproof fabrics by treating them with a solution of a fatty acid derivative of cellulose, followed by treatment with a solution containing a salt of aluminium decomposed by heating. A suitable cellulose derivative is that obtained by treatment of cellulose with caustic soda and chloroacetic acid.

H. Pomeranz[62] gives qualitative tests for dextrin suitable for cloth dressing.

N. J. Planowsky[63] describes a series of experiments on the colloidal properties of the assistants used in finishing fabrics. The Tate electrolytic waterproofing process is described by H. J. M. Creighton.[64]

The effect of fireproofing agents on the durability of cotton fabrics forms the subject of an article by R. L. Sibley.[65] A useful article on the preparation of cloth for finishing is given by S. H. Higgins and A. Hodge.[66] A. Jackman[67] describes the methods of finishing fine woollen and worsted fabrics. The defects produced by finishing are enumerated by E. Midgley.[68]

For protecting wool and fur against the action of moths Bayer u. Co.[69] make use of silicofluoric acid and other complex acids and their salts, which are precipitated by metallic compounds.

In a later patent[70] mention is made of silicofluoric acid, phosphotungstic acid, titanium-hydrofluoric acid, and hydrofluoric acid, which are applied to wool from a cold bath containing assistants such as salts, acids, or mordants. The same company[71] mention numerous organic compounds for protecting wool from moths.

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[58] E.P. 156,514 ; *J.* 1922, 367A.

[59] E.P. 175,746 ; *J.* 1922, 289A.

[60] H. Forster, E.P. 162,627 ; *J.*, 1922, 291A.

[61] G.P. 347,014 ; *J.*, 1922, 290A.

[62] *Monatsch. Textilind.*, 1922, **37**, 14, 33 ; *J.*, 1922, 411A.

[63] *Ber. Polyt. Iwanowo Wosniessensk*, 1921, **4**, 129 ; *J.*, 1922, 749A.

[64] *J. Franklin Inst.*, 1921, **192**, 497 ; *J.*, 1921, 842A.

[65] *J. Ind. Eng. Chem.*, 1921, **13**, 676 ; *J.*, 1921, 806A.

[66] *J. Soc. Dyers and Col.*, 1922, **38**, 196.

[67] *Ibid.*, 1922, **38**, 173.

[68] *Ibid.*, 1922, **38**, 180.

[69] G.P. 347,723 ; *J.*, 1922, 541A.

[70] G.P. 347,849 ; *J.*, 1922, 541A ; *cf.* E.P. 173,536 ; *J.*, 1922, 138A

SIZING.

Animal size or casein used for sizing of yarns or the stiffening of fabrics is hardened by treatment with 2% of methylol formamide, $H.CO.NH.CH_2.OH$.[72]

TESTING.

H. Alt[73] describes a series of tests on the effect of water and of the bacteria present in soil on the strength of various fabrics. Koehler and M. Marqueyrol[74] describe a method of determining the copper member of cellulose in which precipitated copper carbonate is used. The cuprous oxide formed is determined by adding excess of iron alum and titrating the ferrous sulphate formed with permanganate.

H. F. Coward and G. M. Wigley[75] give a method for detecting and determining acidity and alkalinity in cotton fabrics, particularly aeroplane fabrics. With regard to tests for oxycellulose, E. Heuser and F. Stöckigt[76] state that on distillation with 12% hydrochloric acid oxycellulose gives carbon dioxide whereas hydrocellulose does not. Oxycellulose prepared by means of acid permanganate, as used by E. Knecht and F. P. Thompson, gave 1·04% CO_2, the maximum amount obtained being 1·32%. As a qualitative test for oxycellulose Tollens' β-naphthoresorcinol test for glycuronic acid[77] is proposed.

E Ristenpart and P. Wieland[78] discuss the effect of formaldehyde on the colour of dyed materials. B. Setlik[79] gives a list of the various tests applied in determining the general fastness of dyed materials.

A method of testing the fastness of colours to light is described by the Atlas Electric Devices Co., Inc.[80] In view of the unreliability of tests made with the quartz mercury lamp there is need for a satisfactory method of testing. The results obtained by the Fade-Ometer are much nearer to those obtained with sunlight than tests made with the quartz mercury light.

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[71] G.P. 344,266, 344,596–8 ; *J.*, 1922, 289A.

[72] E.P. 156,514 ; *J.*, 1922, 367A.

[73] *Textilber.*, 1921, **2**, 301 ; *J.*, 1922, 51A.

[74] *Mém. Poudres*, 1921, **18**, 78 ; *J.*, 1922, 323A.

[75] *J. Text. Inst.*, 1922, **13**, 212 ; *J.*, 1922, 497A.

[76] *Cellulose-Chem.*, 1922, **3**, 61 ; *J.*, 1922, 583A.

[77] *J.*, 1908, 716.

[78] *Textilber.*, 1922, **3**. 397 ; *J.*, 1922, 895A.

[79] *Chim. et Ind.*, 1922, **8**, 541 ; *J.*, 1922, 891A.

[80] *J. Soc. Dyers and Col.*, 1922, **38**, 285.

ACIDS, ALKALIS, SALTS, ETC.

By H. J. BAILEY, O.B.E., F.I.C.,

Inspector of Alkali, etc. Works.

As pointed out in last year's Report, the heavy chemical industry was passing through a very severe strain of depression during the year 1921, and the year now under review opened with this industrial depression almost at its worst; stocks of raw materials had fallen seriously in value, while stocks of finished products could not readily be disposed of. The early months of the year were marked by strenuous efforts to cut down expenses and to reduce costs of production, and the year as a whole has been one of great anxiety to all those engaged in chemical manufactures under the above heading. As the year progressed, however, industry began slowly to revive, and, although even at the end of the year activities had not yet reached the normal, the outlook for the future is more reassuring.

The anticipated keen competition in ammonia products, which caused such serious depression in prices at the commencement of the year as to rule out the possibility of the smaller works maintaining any profit on manufacture, has not materialised to the extent forecasted; nitrate of soda stocks have been largely liquidated, and a steady demand maintained for sulphate of ammonia. Germany has required practically all her own production of nitrogeneous fertilisers, and at the end of the year was endeavouring to negotiate for a supply of Chilian nitrate.

The production of sulphuric acid in the United Kingdom is a very sure guide to the activities of the heavy chemical industry, and for the years 1919–21 was approximately as follows :—

Sulphuric acid manufactured in the United Kingdom, expressed as tons of 100% H_2SO_4.

	1919.	1920.	1921.
Chamber process	850,000	987,000	533,000
Contact process	33,000	66,000	28,000
Total	883,000	1,053,000	561,000

It is not possible at the time of writing this review to give an accurate estimate of the production for the year 1922, but it is anticipated that the figure will be about 800,000 as tons of 100% H_2SO_4, of which about 40,000 tons will be contact process acid.

Safeguarding of Industries Act.

The attempt made by the Government, under the above Act, to foster certain branches of the chemical industry which might otherwise be liable to extinction, has led to considerable discussion during the year, and several important questions have been argued before the Official Referee, definite decisions in certain cases being given. The question of the meaning of the term "Fine Chemical" was discussed at Nottingham,[1] and an attempt made to arrive at a definition. A complaint that calcium carbide[2] was improperly excluded from the list of articles covered by the Act was rejected by the Referee. Discussion of the terms "Fine Chemical" and "Synthetic Organic Chemical" took place at Newcastle.[3] Complaints were lodged against the inclusion of cream of tartar, tartaric acid, and citric acid,[4] and the meaning of the term "Fine Chemical" was argued before the Referee; the complaints were upheld in the decision and these substances consequently were removed from the list. In his decision the Referee emphasised the importance of trade usage or classification where such existed. The exclusion of sulphur dioxide[5] (liquid) from the list of articles was upheld. The lists were amended by the inclusion of "mechanical aggregates of oxide of thorium and oxide of cerium and of nitrate of thorium and nitrate of cerium being ingredients of incandescent gas mantles."[6] Boric acid[7] was removed from the list of articles included under the terms of the Act. Sodium hyposulphite "R"[8] was included in the original list, and after argument before the Referee complaint to have this article removed failed, but the words "photographic quality" were inserted in the list to define its purity.

BRITISH INDUSTRIES FAIR.

At this Exhibition[9] at Shepherd's Bush, in the early spring, the heavy chemical industry was well represented, and this no doubt helped to advertise the great progress made in applied chemistry in this country since the outbreak of war. A large range of exhibits was shown, and this was followed in March by the distribution of a list of Fine Chemicals[10] produced in this country. This list, issued by the Association of British Chemical Manufacturers, contained the names and addresses of thirty-eight manufacturers, with some 1700 products produced by them.

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[1] *J.*, 1922, 24R, 48R.
[2] *J.*, 1922, 44R.
[3] *J.*, 1922, 71R.
[4] *J.*, 1922, 115R.
[5] *J.*, 1922, 148R.
[6] *J.*, 1922, 227R, 239R.
[7] *J.*, 1922, 287R.
[8] *J.*, 1922, 309R.
[9] *J.*, 1922, 92R.

SMOKE AND NOXIOUS FUMES.

Considerable attention has been paid during the year to the question of the abatement of smoke and noxious vapours. The report of the Committee appointed to consider this question, of which Lord Newton was the chairman, was issued at the end of last year.[11] In this report the question of industrial and domestic smoke is dealt with, and recommendations were made for future legislation with a view of obtaining more uniform methods of dealing with industrial smoke by county councils or county boroughs, under the supervision of the Ministry of Health; also it was recommended that noxious vapours should be dealt with by a further extension of the Alkali etc. Works Regulation Act, 1906, where such extension is found necessary. No legislation has resulted during the year under review to give effect to any of these recommendations.

H. J. Bush[12] gave a valuable paper on electrical precipitation as applied to the removal of acid fume from gases resulting from the concentration of sulphuric acid, also for the removal of dust containing potash salts from gases emitted by blast-furnaces; he also discussed electrostatic precipitation as applied to the cleaning of roaster gases from mechanical pyrites furnaces. The paper dealt with the Lodge and the Cottrell designs of both the plate type and rod and tube type, and showed how electrical precipitation is being extended to displace cyclone or bag dust collectors to deal with the air from dusty operations. A flue type of precipitator has been installed to deal with chloridised vapours from the furnacing of mine tailings, where gold, silver, mercury, and lead are being recovered. The difficulties of standardising plant of this type were pointed out, as every individual installation has to be designed to deal with the particular problem in hand. In the tube type, with a tube of 12 in. diameter, the voltage required as measured by the spark-gap meter, was in the neighbourhood of 50,000, and the upward or downward passage of the gases was discussed.

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[10] *J.*, 1922, 101R.

[11] *J.*, 1922, 1R.

[12] *J.*, 1922, 21T.

Progress in electrical precipitation has been more rapid in America and on the Continent than in this country; there are now, however, several installations working on dust removal, and during the year a further plant to deal with dust from pyrites burners and acid mist in the contact process has come into operation in this country, with satisfactory results.

W. E. Gibbs[13] dealt with the industrial treatment of fumes and dusty gases. In a valuable survey of the subject he pointed out that smoke, fumes, and dusty gases can all be regarded as disperse systems, in which the dispersed system is a solid or liquid, and the dispersion medium a gas. Particles larger than 10^{-3} cm. diameter settle in still air with increasing velocity, particles of 10^{-3} to 10^{-5} cm. diameter settle in still air with a constant velocity according to Stokes' law, and do not diffuse; while smokes, the particles of which range from 10^{-5} to 10^{-7} cm. in diameter are in active Brownian movement, do not settle in still air, and diffuse fairly rapidly. The methods of facilitating the settlement of dust were dealt with, namely: (*a*) by retarding the rate of flow of the gases by means of cooling, passing through flues of large cross-sectional area, and by baffling; (*b*) by shortening the vertical path to be traversed by the particles; (*c*) by centrifugal action such as in the cyclone dust catcher; (*d*) by loading the particles with water either by cooling or by means of an atomised water spray.

Filtration methods were also dealt with, including the Halberg-Beth system of bag filtration as applied to blast furnace gases. The question of smoke washing was discussed and the difficulty of obtaining intimate contact of the particles with water was pointed out; electrostatic precipitation was referred to, and suggestions were made for further research work on the subject.

ERNEST SOLVAY.[14]

The death occurred on May 26th, 1922, of Ernest Solvay, and thus was removed one of those personalities whose work had marked a distinct epoch in heavy chemical manufacture. The Leblanc process of manufacture of sodium carbonate had held the field from 1790 until 1863, when Solvay established the ammonia-soda process at Charleroi, which after initial struggles has become world wide; so that in 1903, some 1,600,000 tons, out of a world's total production of 1,700,000 tons, was made by the ammonia-soda process. At the present time this process is gradually being replaced by the electrolytic decomposition of sodium chloride, but for over 50 years the Solvay process has been the basis of the enormous increase in heavy chemical manufacture.

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[13] *J.*, 1922, 189T.

[14] *J.*, 1922, 231R.

EVAPORATION.

J. W. Hinchley[15] contributed to the knowledge of this subject—one of considerable importance in heavy chemical manufacture. He pointed out that the subject must be considered under two headings: (*a*) evaporation below the boiling point of the liquid evaporated, and (*b*) evaporation at the boiling point. Under class (*a*) the rate of evaporation may be taken as approximately proportional to the area of surface exposed, and the rate of evaporation may be expressed by the formula :—

$$\text{Rate of evaporation in kilograms per sq. metre per hr. from water surfaces} = \left(\frac{p_e - p_d}{50}\right)^{1 \cdot 2}$$

where p = vapour pressure of the liquid in mm. of mercury and p_e = vapour pressure of water vapour in the air in the same units. This formula was tested with salt solutions and compared with factory results, and was found to give results about 10% high, owing to the fact that still air is impossible above a warmed liquid owing to convection currents. The work of Leonard Hill and Carrier on the same subject was referred to, and formulæ were given for the effect of air currents impinging on the surface of the evaporated liquid.

The measurement of vapour pressure in air was dealt with, and the application of the formula to drying operations in air dryers was pointed out. Under class (*b*), evaporation at the boiling point, the above equation breaks down when p_e equals the barometric pressure, but in still air, without any disturbance of the surface, it is suggested that the rate of evaporation would be about 26 kg. per sq. metre per hour. This figure indicates the rate from any water solution where no difficulties from frothing or entrainment would occur. It was pointed out that maximum rate of evaporation from boiling liquids was difficult to determine, but a figure of 250 kg. per sq. metre per hour was suggested, though for rectifying plant where entrainment must be avoided the figure of 100 kg. should not be exceeded and plant should be designed accordingly. The rate of heat transmission and the temperature drop were shown to have a distinct effect on the rate of evaporation. Scale, material, multiple evaporation and the heat pump were also discussed.

FIXATION OF NITROGEN.

J. A. Harker[16] gave a valuable summary of the post-war progress in nitrogen fixation before Section B of the British Association at Hull. The arc process, which was put into commercial operation in Norway in 1904, has now reached enormous development. As pointed out in the Report of the Nitrogen Products Committee,[17] although power requirements are large it is still the cheapest known method for the synthetic manufacture of nitirc acid. At Notodden plant is now installed to utilise 45,000 kilowatts, and at Rjukan furnaces employing 200,000 kw. have been erected, this energy being derived from water power. At Rjukan II. a 15,000 kw. steam-operated set has been erected to utilise waste steam produced by the boilers, which are adapted to act as coolers for the process gases which leave the furnaces at about 1000° C. In the arc process only about 2% of the electrical energy is actually absorbed in the initial oxidation of nitrogen, and the concentration of nitric oxide in the gases leaving the furnaces is only 1·2%. Suggestions for improving the yields have been along the lines of enriching the air with oxygen up to a 50% content in a closed circuit, the product being removed as liquid nitrogen peroxide by cooling, instead of by the method of absorption towers. Experiments led to considerable increase of output under certain conditions, yet serious difficulties were encountered and several explosions have occurred at works in Switzerland and Germany where this was being tried. The nitric acid works on the Birkeland-Eyde system erected during the war in France are now closed for the power to be used for railway electrification, as originally intended.

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[15] *J.*, 1922, 242T.

[16] *J.*, 1922, 387R.

[17] *J.*, 1920, 25R.

Synthetic Ammonia Process.

The synthetic ammonia process originally worked out by Haber and his colleagues and installed by the Badische Co. as Oppau and later at Merseberg, is not to-day the only process for the synthesis of ammonia from its elements, as shown in the table on page 168.

The original German process operated at pressures of 200 atmospheres, but to-day, pressures up to 1000 atmospheres, or about 7 tons to the square inch, are utilised as in the Claude[18] process. The plant at Sheffield, Alabama, is now closed down; at this works activated sodamide was used as a catalyst material, but this was difficult to prepare in bulk, and though its activity was fairly high at first, it was permanently destroyed even by small quantities of water vapour. Claude is now using a new form of catalyst tube made in Sheffield, of a new material having remarkable properties at high temperatures, and which promises to give a safe industrial life much longer than anything previously attained. Whereas in the Badische process the cost of preparing the hydrogen used amounts to 65—70% of that of the ammonia produced, Claude[19] is devoting attention to the production of cheap hydrogen from the gases from the coke ovens at Bethune. In the Casale process as now running at Terni, near Rome, hydrogen is obtained

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[18] *J.*, 1921, 420R.

[19] *J.*, 1922, 393R.

Forms of the Synthetic Ammonia Process.

Country and date.		Process.	Operating pressure in atmospheres.	Approx. space-time yield, kg. lit. cat. hr.	Approx. percentage concentration NH_3.	Method of removing NH_3.	Source of hydrogen.	Remarks.
Germany	(1913)	Haber-Bosch (Badische Co.)	200	0·3 to 0·5	7–8	(*a*) Cooling (*b*) Solution in water.	Water gas catalytic process.	Very large units, low gas velocity, criculation. Preheating. Process in large scale operation.
England	(1917)	M. of Munitions (Greenwood and associates).	150	5–20	2–4	Solution with temp. cycle.	do.	Much higher gas velocity; some electric heating. Experimental scale only.
„	(1921)	Synthetic Ammonia & Nitrates, Ltd., Billingham.	—	—	—	—	—	Experimental plant working 2 tons per day.
U.S.A.	(1918)	General Chemical Co. (Sheffield, Alabama).	under 100	about 0·4	8	Cooling to 30° or 40° C.	Water gas catalytic process.	U.S. Govt. Works, designed for 11,000 tons N annually. Not now in operation.
	(1920)	Atm. Nit. Corp. Solvay Process Co., Syracuse.	—	—	—	—	—	Working on a scale of 10 tons NH_3 per day. Circulation.
France	(1920)	Claude ..	900–1000	about 5	25	Condensation at atm. temp.	Various.	Working on scale of 5 tons a day. Three stages in series. No circulation.
Italy	(1922)	Casale (Soc. Idros Terni)	about 500	—	—	Solution.	Electrolytic.	Working on a scale of about 4 tons per day. Circulation.
„	(1922)	Pfauser ..	—	—	—	Solution.	Electrolytic.	—
Norway	(1921)	Cederberg ..	—	—	—	—	—	—

electrolytically from large cells operated by power from waterfalls near by; some of this hydrogen is burnt in air to give the desired mixture of hydrogen and nitrogen, and further attention is being given to the bulk generation of electrolytic hydrogen.

Cyanamide Process.

This process, though stated by many authorities to be obsolete, had at the end of the war an aggregate capacity in tons of nitrogen greater than that of any other process. The largest plant in the world, that erected during 1918, to produce 200,000 tons annually, at Muscle Shoals, U.S.A., is idle, and no forecast as to its future can be made, but plans are on foot for doubling the plant of Frank and Caro, at Presteritz. An American company is now manufacturing from cyanamide a mixed fertiliser in the form of mono-ammonium phosphate, but this would appear to be too costly for many applications. Independent investigators in Sweden and Switzerland have succeeded in working out processes whereby, by the action of carbon dioxide, free cyanamide is first formed from the calcium salt and subsequently transformed to urea. In the Swiss form of the process excess of sulphuric acid employed in the second stage is utilised in action upon phosphate rock, when a neutral fertiliser termed "Phosphazote" is produced, having its nitrogen in the form of urea. The proportions of the constituents can be varied within limits, but as usually produced, the product contains about 11—12% of nitrogen as urea and about the same percentage of phosphoric anhydride.

Cyanide Process.

Experiments are still being continued in this country, and in America cyanide is being made on a considerable scale from cyanamide as a source of hydrocyanic acid for plant fumigation. The costs of producing cyanide by existing methods are said to be excessive and further research is required into the reactions involved in the preparation of sodium cyanide.

In the report of the British Sulphate of Ammonia Federation[20] it is stated that Germany was consuming 320,000 tons of nitrogen annually for agricultural purposes, or about 10·3 lb. per acre, as against 2·0 lb. in France and 4·5 lb. in England. These three countries together consume some 404,300 tons of nitrogen, and it was pointed out that there was considerable scope for increase in consumption in the two latter countries.

The real cause of the Oppau explosion is still shrouded in mystery, although an exhaustive enquiry was held by a Parliamentary committee, and much expert evidence was called.[21] The Prussian Minister of Trade has issued a notice[22] stating that a mixture of equal parts of ammonium nitrate and sulphate can be exploded by means of a picric acid primer with a very strong initial detonation, and blasting is to be avoided in the case of fertilisers containing ammonium nitrate wherever possible. A preliminary communication by A. Findlay and C. Rosebourne[23] on the decomposition and stabilisation of ammonium nitrate in the presence of an oxidisable material, such as starch or woodmeal, indicates that the addition of carbamide (urea) in relatively small amounts to the mixture has a considerable stabilising effect.

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[20] *J.*, 1922, 514R.

Synthesis of Ammonia.

Various patents for improvements in the Claude process have appeared, including suggestions for suitable control of the temperature of the reacting gases,[24] for checking bursting of the reaction tubes by immersion of the tubes in kieselguhr,[25] for utilising gases from coal distillation plant and water gas produced by acting on the hot coke with superheated steam,[26] also for employing part of the hydrogen, after separation by a solution method, with air in a gas engine to obtain the necessary nitrogen-hydrogen mixture for the reaction. A catalytic material[27] made from ferrous oxide and molten iron by directing a jet of oxygen into the molten mass in a magnesia crucible, gives good results, but has a life of only 10–15 hrs.; the addition of 5–10% of lime and a small proportion of alkali oxide to the melt produces a material lasting some hundreds of hours and giving a 40–50% conversion. By cooling coke-oven gas, freed from constituents other than hydrogen, methane, nitrogen, and carbon monoxide, it is claimed that hydrogen suitable for ammonia synthesis can be prepared[28]; the cooling is effected gradually in three stages between -160° C. and -210° C., no freezing occurring owing to the miscibility of the liquids.

Nitric Acid Synthesis by Gaseous Explosions.

F. Häusser[29] contrasts the explosion process with the cyanamide process, arc process, and synthesis of ammonia, and starting from a theoretical basis describes laboratory experiments and the working of a large-scale plant. Experiments were carried out on

[21] *J.*, 1922, 451R.

[22] *J.*, 1922, 62R.

[23] *J.*, 1922, 58T.

[24] E.P. 150,744; *J.*, 1922, 99A.

[25] *J.*, 1922, 140A, 590A.

[26] E.P. 156,135; *J.*, 1922, 173A.

[27] E.P. 153,264; *J.*, 1922, 215A.

[28] E.P. 174,327; *J.*, 1922, 463A, 670A.

[29] *J.*, 1922, 253R.

compressed mixtures of air with coal gas, and air with carbon monoxide, in the first place in a small bomb of 552 c.c. capacity, and later in one of 1651 c.c. capacity, changes in the equilibrium mixture being avoided by quickly cooling the gases with a water spray. These experiments showed that yields increase with the size of the bomb, the larger unit giving yields 90–120% above the theoretical. On passing to works scale experiments the water spray was abandoned on account of severe corrosion, and the gases were cooled by expansion immediately after the explosion, the exhaust gases being swept out of the bomb by means of air, as any residual exhaust gases remaining in the bomb lower the temperature of the explosion with reduction of yield. The first experimental plant contained a bomb of 100 litres capacity and worked on coal gas and air, giving an exhaust gas containing 8-9 grams of nitric acid per cb. metre. Yields decreased if combustion was incomplete, the carbon monoxide presumably reducing the nitric oxide. Coke-oven gas taken after the benzol plant, that is, with the usual by-products removed, was freed from sulphur by cleaning boxes, passed through a meter to a small gas-holder, and thence forced into the gas chamber by the compressor. The air was forced into the air vessel, and thence to the bombs after being preheated to 300° C. by a superheater coil heated by the exhaust gases. The gas and air were compressed to 5·5–6·0 kg. per sq. cm., and after the explosion the bomb was scavenged with air at 0·75 kg. per sq. cm., which passes to a separate vessel. A Linde oxygen plant was tried for enrichment, but was found unnecessary and the process simplified, as the nitric oxide content of the exhaust gases was sufficient to give a suitable strength acid on absorption in suitable towers. Mixing of the gases took place on entering the bombs, which were provided with specially designed inlet valves. Back pressure valves were provided to prevent an excess of air and gas entering the pressure vessel, and avoid any danger of mixing taking place outside the bombs, and a lead membrane ensured safety in case of pre-ignition, which must be avoided in the inlet tubes. The usual Bosch ignition was employed, and the exhaust valve opened about 0·15 sec. after the explosion, pressures up to 25 kg. per sq. cm. occurring during the explosion. In each bomb, of which two were of 100 litres and a later one of 300 litres capacity, there were 44 to 45 ignitions per minute. The exhaust gases passed through the fire-tube of a marine boiler, and were cooled to 250° C., only iron apparatus being used up to this point. After leaving the boiler, further condensation was effected in aluminium coolers, and from thence the gases passed to alternate oxidation and absorption towers, the space required being calculated according to Bodenstein's[30] researches. Figures are given of the monthly averages, which indicate that results are considerably better with the bomb of larger size, and yields of about 100 grams of HNO_3 per cb. m. of coke-oven gas are claimed.

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[30] *Z. Elektrochem.*, 1918, 24, 183.

C. J. Goodwin[31] in a paper before the British Association indicates that impending trials of the Häusser process in a 1200 to 1500 litre bomb are likely to lead to commercial yields; modern alloys and unstainable steel have assisted in overcoming corrosion difficulties, and the volume of the absorption towers has been reduced to one-sixtieth of the normal by the use of chromium-nickel-steel or silicon-iron towers and absorption under 2½ to 4 atmospheres pressure, and a yield of 150 grams of HNO_3 per cb. m. of coke-oven gas is anticipated.

Ammonium Compounds.

Considerable progress has been made during the year in regard to the production of dry neutral sulphate of ammonia for commercial purposes, and several further patents have been taken out. J. B. Hansford[32] produces a neutralised salt by the use of two saturators; in one, which can be closed, the acid is only partly neutralised, and residual gases from the final saturator pass through for absorption of any remaining ammonia when saturation point is being reached there. The second or final saturator is fed from the contents of the first saturator, and is then neutralised by passing the ammonia steam from the still in the usual way, suitable cocks being provided so that the still gases can be fed to one or both saturators as desired. A special rotating table for drying the salt, provided with gas burner heaters, delivers the salt to bags in an excellent condition. The South Metropolitan Gas Co. and P. Parrish[33] patent the process of working two saturators, one from the free and the other from the fixed ammonia portions of the still, final neutralisation being effected in that from the fixed portion. In this way pyridine evolutions and discoloration of the salt are said to be avoided. A further patent[34] for producing ammonia liquor of suitable strength for washing the crystals is also taken out by the same authors. R. Lessing[35] removes the crystals to a lagged draining vessel heated by low-pressure steam prior to drying in the centrifuge. D. Thickins and The Ebbw Vale Steel Co.[36] patent a method of drying and neutralising the salt in a tower fitted with shelves and rotating scrapers, down which the salt passes, meeting an upward stream of hot air and ammonia gas. G. Weyman[37] treats the salt in the centrifuge when partially dried with powdered ammonium carbonate, and claims that a salt containing over 25·5% NH_3 can be made without special drying. W. C. Holmes and Co., W. G. Adam, and C. Cooper[38] patent a method for drying and neutralising the salt as usually made by passing it through a closed inclined cylinder fitted with twin-screw worms, the cylinder being partially encased in its upper portion by an air jacket heated by a gas burner, through which heated air can be drawn into the cylinder by fan or steam injector draught. Ammonia gas is led into the cylinder and any excess withdrawn with the heated air through an acid wash before discharge to the air.

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[31] *J.*, 1922, 394R.
[32] E.P. 173,818; *J.*, 1922, 173A.
[33] E.P. 176,977; *J.*, 1922, 371A.
[34] E.P. 177,726; *J.*, 1922, 372A.
[35] E.P. 178,046; *J.*, 1922, 414A.
[36] E.P. 181,884; *J.*, 1922, 631A.

P. Parrish[39] gave a valuable contribution, summarising existing knowledge in regard to design and working of ammoniacal liquor stills, and pointed out the necessity for due consideration to be given to the bubbling arrangements for the steam in relation to vapour tension, and vapour velocity, with a view to economy in steam consumption; he also indicated the need for more complete utilisation of the waste heat leaving the saturators. Details of the running of an experimental plant were given, the feed-liquor being varied while the steam consumption remained constant, which pointed to the fact that, given sufficient time contact in the size of still and number of trays, the steam consumption can be made to approach a minimum for a given liquor feed; experiments were also carried out to show the relative capacity of the still with varying strengths of feed liquor while the percentage of ammonia in the waste liquor was maintained at a constant figure, which proved that capacity increased in a fairly definite ratio with strength of feed-liquor.

T. Lewis Bailey[40] states that there is an increasing number of cases where difficulty is being experienced in the disposal of the waste liquors from the distillation of ammoniacal liquor from gas or coke-oven works. Methods of disposal in general use include: (i.) admission to sewers under controlled conditions; (ii.) utilisation on the works by various means, including the pumping of the effluent over spoil heaps or into old colliery workings; (iii.) chemical treatment and decolorisation with SO_2 gases (none of these latter processes has been of great practical value); (iv.) bacterial treatment on filter beds; much work was done on this by G. J. Fowler[41] and colleagues, but the process as applied to works practice has not proceeded beyond the experimental stage. The total volume of effluent liquor produced by a still fed with 8-oz. liquor (1·7% NH_3) would be theoretically 4900 gallons per ton of sulphate made, and 50% increase of volume is suggested for condensed steam, lime water, etc. H. Maclean Wilson gives an approximate figure of 9000 to 10,000 gallons per ton of sulphate as common coke-oven practice where the feed-liquor would probably only contain about 1% NH_3. From investigations carried out on spent liquor by F. W. Skirrow[42] and by G. J. Fowler, E. Ardern, and W. T. Lockett,[41] and by P. F. Frankland and H. Silvester[43] it would appear that the most noxious constituent of these spent liquors from the point of view of disposal to sewage works was the phenol constituent, the effect on the oxygen absorption test being far greater by this constituent than that of thiocyanate. It is pointed out also that the phenol content of the so-called "devil liquor" is much higher than that of the ordinary spent liquor, and in certain samples some 50% of the total phenol content of the ammonia liquor distilled was found in the devil liquor. Experiments were carried out to determine the volatility of the phenol content when the effluent liquor was passed down a brick-packed tower, up which were passed hot boiler flue gases; the results indicate that at suitable temperatures and with the requisite amount of flue gases some 90% of the phenol content may be removed in this way. An experimental works plant has been in operation at Hornsey Gas Works, and further plants of this type are foreshadowed.

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[37] E.P. 183,089; *J.*, 1922, 669A.

[38] E.P. 187,035; *J.*, 1922, 982A.

[39] *J.*, 1922, 229A.

[40] *58th Rept. of Chief Inspector of Alkali etc. Works*, 1921; *J.*, 1922, 316R.

[41] *J.*, 1911, 174.

H. M. Lowe[44] describes a method of determining approximately the ammonia content of spent liquors by means of a special form of gas analysis pipette. Sodium hyprobromite is added to 20 c.c. of the sample and quickly shaken and the evolved gas measured; in this way determinations can be made without distillation in about five minutes.

A communication by G. E. Foxwell[45] on the thermal dissociation of ammonia with special reference to coke-oven conditions dealt with the decomposition of ammonia in the presence of coal-gas. Experiments were carried out by passing the mixed gases through a silica tube packed with different materials, and also when the tubes were empty, at different temperatures. The influence of firebrick material, coke-ash, and chlorides, was studied, and various deductions were made therefrom. The velocity of decomposition is stated to increase slowly with the rise of temperature; iron, especially in the brickwork, is said to be very deleterious, while the presence of salt appears to retard the rate of decomposition.

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[42] *J.*, 1908, 58.
[43] *J.*, 1907, 231.
[44] *J.*, 1922, 11T.
[45] *J.*, 1922, 114T.

OXIDATION OF AMMONIA.

C. S. Piggot[46] gives details of the preparation of manganese catalysts, and states that over 90% efficiency can be obtained at 800° C. with a mixture of finely-divided manganese dioxide with 40% of copper oxide.

C. S. Imison and W. Russell[47] gave valuable details of the practical application of the oxidation of ammonia to the supply of nitrogen oxides for chamber acid plants. The reaction (i.) $4NH_3+5O_2=4NO+6H_2O$ is the one aimed at, though with deficiency of air the reaction may take the form (ii.) $4NH_3+3O_2=2N_2+6H_2O$; for the first reaction about 6 vols. of air per vol. of NH_3 is required theoretically, but in actual practice such a ratio leads to loss of ammonia as nitrogen as in the second equation, and a proportion of 9 vols. of air to 1 of ammonia gives the best results. Oxidation begins with platinum at about 650° C., and a 10% ammonia mixture will theoretically yield a temperature below 700° C., according to equation (i.), and over 900° C., according to equation (ii.), consequently it is usual to sacrifice efficiency to a slight degree in order to maintain the temperature at a point where the catalyst works best. The history of the process was discussed, and data given of the experimental difficulties encountered since 1916, when the process was first tried commercially in this country. A full description was given of the type of plant now found to be most suitable. Commercially pure 25% ammonia liquor from coke or gas works has been used as the source of ammonia; this is distilled in a simple form of coke-packed still, the liquor being introduced one-third of the way down the still, the space above this inlet being to some extent a dephlegmator to prevent too much moisture passing forward with the ammonia. Air is admitted below a perforated plate one-third from the bottom of the still, this plate carrying the packing, and the still is provided with dry and live steam. It was found that small quantities of sulphides up to 0·034% $(NH_4)_2S$ or traces of pyridine had no serious effect in poisoning the catalyst, and the original soda wash for the mixed gases was cut out. The gases from the still pass through a glass wool filter contained in a lead box and are conveyed by lead pipes right up to the converter. The chief troubles experienced in poisoning of the catalyst were found to be due to dust or rust carried forward on to the gauze, and converters were eventually made of enamelled iron and placed so that the platinum gauze was vertical, and later an enamelled iron heat interchanger was attached to the converter so as to raise the temperature of reaction and thereby increase the rate of conversion on the gauze. Accurate regulation of the ammonia and air supply is the chief requirement of the process, and a simple method of testing the ammonia liquor feed to the still was devised, by timing the filling of a sight vessel, the air-regulating valve being controlled by manometer readings; these two measurements were correlated on a chart for a given desired strength of gas. This simple arrangement enables the man in charge of the sulphuric acid plant to increase or decrease the nitre to the acid plant at will, without interfering with the efficiency of the catalyst. By preheating the gases to 300° C. it has been possible to increase the capacity of a 6 in. × 4 in. gauze to at least the equivalent of 50 cwt. of nitrate of soda per week, and maintain a 93% efficiency of conversion. Loss of platinum on the converter is given as 0·002 to 0·004 oz. troy per ton of 100% nitric acid produced. Figures were given for capital and working costs, and it was claimed that a saving had been effected as compared with the former nitre-pot process of nitration. The working of plant for the manufacture of nitric acid was also described on similar lines, and the advantage of absorption of the final gases in concentrated sulphuric acid was pointed out, also the method of recovery of a high strength nitric acid by means of addition of concentrated sulphuric acid and distillation of the nitric acid from denitration towers. This contribution marks a decided step forward in the application of ammonia oxidation to the heavy chemical industry, and the authors are to be congratulated on the clarity and detail with which they have treated the subject.

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[46] *J. Amer. Chem. Soc.*, 1921, **43**, 2034; *J.*, 1922, 96A.

[47] *J.*, 1922, 37T.

E. Decarrière[48] notes the serious poisoning effect of small traces of hydrogen phosphide on the platinum catalyst, and states that impurities of only 0·00002% reduce the oxidation by nearly 30%. The catalyst is stated to revive after the impurity is removed, but regeneration is slower the greater the amount of impurity originally present.

H. A. Curtis[49] states that an alloy of 1% iridium with platinum was found to be as efficient a catalyst as pure platinum, and that the highest efficiencies (over 90%) were obtained with gauze temperatures of 800°–880° C., but this cannot be maintained without auxiliary electrical heating unless heat interchangers are adopted.

NITRIC ACID.

A communication by J. A. Hall, A. Jacques, and M. S. Leslie[50] on the working of absorption towers for nitric acid condensation was published. The rate of flow of the nitrous gases and the condensing liquors was studied, and also the effect of addition of air, and from the experimental work mathematical calculations were deduced to express the amounts of absorption and oxidation

[48] *Comptes rend.*, 1922, **174**, 460; *J.*, 1922, 214A.

[49] *Chem. and Met. Eng.*, 1922, **27**, 699; *J.*, 1922, 896A.

[50] *J.*, 1922, 285T.

taking place under given conditions of velocity and concentration of the gases, and of flow and concentration of the absorbing fluid. From these calculations were deduced the optimum ratio between absorption and oxidation spaces under such conditions, and indications were given as to how the deductions arrived at might be utilised in designing sets of absorption towers.

A further publication by the Ministry of Munitions and Department of Scientific and Industrial Research in No. 7 of the Technical Records of Explosives Supply, 1915–1918[51] gives full records of the manufacture of nitric acid at the Government factories during the war. This record gives an excellent summary of large-scale nitric acid manufacture from nitre and sulphuric acid and is a valuable contribution to the technical literature on the subject.

ACID MIXING.

Valuable data have been published during the year in connexion with the mixing of nitric and sulphuric acids for explosives manufacture. In No. 4 of the Technical Records of Explosives Supply[52] a record is given of acid mixings, chiefly in connexion with TNT manufacture. The record is divided into three sections; (1) Acid cycles, acid balances, and control of plant output; (2) The position of acid-mixing plant in the acid cycle and procedure adopted in mixing; (3) Plant and process for acid mixing. The strength of spent acid and procedure followed in working off weak nitric acid are also dealt with; and acid mixes, acid dopes, and practical methods of calculation regarding the same are discussed.

J. W. McDavid[53] contributed data on the heat developed in mixing various strengths of nitric and sulphuric acids, and produced curves from which the heat generated in the production of mixed acids for explosives manufacture can be readily calculated. The same author[54] gave a rapid and accurate method for the calibration of storage tanks. The method is dependent on the principle that water, flowing through a tube or orifice under a constant head, gives a constant rate of flow. A simple form of portable calibrator was designed which could be fitted readily over any tank, and coupled to a water supply by means of hose-pipe, and gave results correct to within 0·02%. This is an ingenious and simple apparatus which should prove of great use in the correct calibration of storage tanks and which is quite independent of the shape of the tank.

W. H Patterson[55] discusses the various methods of testing mixed acid, and states that total acid can be most readily determined by direct titration with caustic soda. For determination of nitrous acid content the permanganate method is recommended for fresh acids or waste acids containing organic matter not readily oxidisable by permanganate, such as from TNT manufacture; but for waste acid from picric acid manufacture containing oxalic acid, the following method is recommended: the sample is added to a strong solution of potassium citrate in a Lunge nitrometer, and a concentrated solution of potassium ferrocyanide added; from the nitric oxide evolved, the amount of nitrous acid is calculated. It is stated that this method tends to give low results. The determination of the total nitrogen acids (i.) by the nitrometer method, and (ii.) by reduction to nitric oxide by ferrous chloride in acid solution, as well as the direct titration of nitric acid with ferrous sulphate, are discussed.

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[51] *J.*, 1922, 429R.

[52] *J.*, 1922, 86R.

[53] *J.*, 1922, 246T.

[54] *J.*, 1922, 295T.

[55] *J*, 1922, 496R.

ANTIMONY SULPHIDE.

A. Short and F. H. Sharpe[56] carried out an investigation into the composition of golden sulphide of antimony as used in the rubber industry, the results of which indicated, according to the authors, that, whilst the presence of antimony pentasulphide was not precluded, the material probably contains no higher sulphide than tetrasulphide, which may be looked upon as either the antimony salt of thio-antimonic acid or as Sb_2S_3,Sb_2S_5. It was also indicated that the sulphur extractable by carbon bisulphide was available for vulcanisation.

D. F. Twiss[57] disagrees with the above authors and refers to Klenker's work in 1899, pointing out that his experiments proved that the slow separation of sulphur from antimony pentasulphide began at 85°—90° C. and that even boiling water caused a liberation of sulphur, and suggests that products of intermediate composition are but mixtures or solid solutions of different proportions of Sb_2S_3 and Sb_2S_5.

HYDROCHLORIC ACID.

B. Neumann[58] states that complete reduction of chlorine to hydrochloric acid, giving a product free from chlorine, is impossible by explosion methods, or by that of Hoppe, but is effected by passing the gas mixture at low velocity over quartz at 380° C. If the quartz is impregnated with magnesium chloride, calcium chloride, or aluminium chloride, the temperatures are reduced to 300°, 305°, or 350° C. respectively. The addition of 1 mol. of water-vapour for each mol. of HCl is necessary and dilution with oxygen has no ill effect.

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[56] *J.*, 1922, 109T.

[57] *J.*, 1922, 171T.

[58] *Z. angew. Chem.*, 1921, **34**, 613; *J.*, 1922, 55A.

A patent for a modification of the Hargreaves process was taken out by T. Godschmidt[59] in which the salt is charged into an unobstructed shaft, passing a bell contrivance, meeting a countercurrent of sulphurous acid, steam, and oxygen introduced through a ring of nozzles situated above the space where the finished sulphate is removed. The hydrochloric acid is drawn off through a ring of nozzles situated at the top of the apparatus by means of a fan and condensed in the usual manner.

INDUSTRIAL HYDROGEN.

A monograph by H. S. Taylor[60] on the above was published by the American Chemical Society, and in reviewing this P. L. Teed gives a useful summary of the efficiencies and composition of the gases as produced by the four main processes in use to-day—namely, electrolysis, reduction of steam by iron (Messerschmitt plant), water-gas liquefaction (Linde), water-gas (catalytic), and indicates that where electricity can be generated from water-power, electrolysis is likely to prove the most efficient.

POTASSIUM AND SODIUM SALTS.

The production of potash in the United States for 1920[61] is given as 166,834 tons of crude material averaging 28·8% K_2O, representing 48,077 tons K_2O, of which 78% was produced from natural brines; imports of potash materials were 982,262 tons containing 224,792 tons K_2O, of which 88% was used for fertiliser purposes. Approximately 50% of the imported potash came from Germany and 23% from France.

Considerable developments in the manufacture of caustic soda along electrochemical lines have taken place in Italy.[62] The difficulties of obtaining fuel during the war, and high prices since the war, have given an impetus to the development of electricity from water-power; the development of the production of electrolytic alkali has followed. At first difficulties were experienced in disposing of the surplus chlorine, but these are now being overcome by utilisation of the chlorine for the manufacture of bleaching powder, synthetic hydrochloric acid (for which purpose hydrogen from the batteries is also utilised), sodium hypochlorite, and zinc chloride, and latterly the production of pure cellulose by the Cataldi process. The Cataldi process consists essentially of the treatment of hemp fibre or other raw material as in Cross and Bevan's analytical method of estimating cellulose, adapted for industrial purposes. A further possible outlet for surplus chlorine is foreshadowed in the use of synthetic hydrochloric acid for the decomposition of the volcanic rocks which are so abundant in Italy and represent the richest and largest source of potassium compounds known. It has been found that finely-divided leucite is readily attacked in the cold by hydrochloric acid, giving a solution of potassium and aluminium chlorides from which crystals containing over 99% KCl can be obtained; semi-industrial experiments are being worked, and it appears probable that considerable development of this source of potash may take place.

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[59] E.P. 150,962; *J.*, 1922, 57A.
[60] *J.*, 1922, 168R.
[61] *J.*, 1922, 8R.
[62] *J.*, 1922, 498R.

Glucina.

A communication by H. T. S. Britton[63] deals with the extraction of glucina from beryl, and the liquid phase relationships of the sulphates of potash, aluminium, and glucinum were studied.

Radium.

A useful process for the recovery of radium from substances such as decayed luminous paint etc., has been worked out by A. G. Francis.[64] The various scrap materials are first roasted, and from the roasted mass scraps of metals such as nails and screws are removed, the mass is then digested successively with sulphuric, hydrochloric, and hydrofluoric acids, and lead sulphate removed by digestion with 30% ammonium acetate solution. The filtrates are treated with barium chloride and dilute sulphuric acid to precipitate traces of dissolved radium sulphate. The radium sulphate and radium barium sulphates are then converted into chlorides by fusion with alkali and treatment with dilute hydrochloric acid. Concentration of the radium is proceeded with by fractional crystallisation, and it was found that better concentration results were achieved from the bromides than from the chlorides. Figures are given of actual recoveries made and it is stated that some 260 mg. of radium has been recovered by the process with a loss of less than 1% during recovery.

Silicious Substances and Silicates.

H. Spence and I. P. Lewellyn[65] patent a method of producing a silicious residue which, when dried and calcined, has certain absorptive and useful properties. The residue is produced during the treatment of certain shales or fireclay for the extraction of alumina with sulphuric acid and contains carbonaceous matter;

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[63] *J.*, 1922, 349T.

[64] *J.*, 1922, 94T.

[65] E.P. 173,799; *J.*, 1922, 174A.

the carbonaceous contents are burnt off by slow combustion in heaps or kilns.

R. Furness[66] deals with the use of sodium silicate as an adhesive, and points out the advantage of silicate over other adhesives, in that it is immune from bacterial activity, and can be made to withstand any particular conditions of temperature and humidity. The sodium silicate of commerce may be considered to be a colloidal solution of silica in Na_2O,SiO_2 or $Na_2O,2SiO_2$ (or both). By varying the proportions of silica to soda content it is claimed that an adhesive can be made suitable to meet all requirements as to viscosity, stickiness, or setting time, and, when used, has the great added advantage of rendering the materials damp-proof and fire-resisting. Silicate adhesives are mainly used in connexion with wood and paper materials, and details are given of its use in the manufacture of built-up paper-board, box-board, etc.

SULPHURIC ACID.

In the report for last year attention was drawn to the fact that in the United States sulphur largely replaced pyrites as a raw material for the manufacture of sulphuric acid during the years 1914 to 1918; acid produced from Spanish pyrites had fallen from 50% of the total in 1914 to as low as 7·6% in 1918. Interesting statistics relating to the world's production and consumption of pyrites and sulphur are given in a pamphlet issued by the Imperial Mineral Resources Bureau,[67] and figures given for the years 1914, 1917 and 1918 for the United Kingdom, as follows :—

United Kingdom.

Year.	Acid made (100% H_2SO_4). Long tons.	Percentage made from				
		Pyrites.		Spent oxide.	Sulphur.	Zinc and copper fumes.
		Imported.	Domestic.			
1914	1,082,000	88·5	0·45	10·6	0·3	0·15
1917	1,382,000	79·9	0·7	11·0	8·1	0·30
1918	1,130,000	79·4	1·6	11·2	7·4	0·40

It should be noted that the increased use of sulphur in the two latter years was mainly due to the operation of the Government

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[66] *J.*, 1922, 381R.

[67] *J.*, 1922, 177R.

Grillo plants designed to burn sulphur only, and not to any material change in trade usage in this country.

The question as to whether sulphur will largely replace pyrites in other countries than the United States is mainly an economic one, but a notable increase in the consumption of sulphur in this country has taken place during this past year, as the following approximate figures for the past few years will show :—

Raw materials consumed for acid manufacture in the United Kingdom. Long tons.

Year.	Pyrites.	Spent oxide.	Sulphur.
1919	588,000	112,000	6,700
1920	686,000	139,000	5,000
1921	313,000	103,000	8,000
1922 (estimate)	390,000	150,000	26–28,000

Whereas during the year 1921, most of the works for the calcination of zinc blende in the United Kingdom were closed down, these works have resumed operations during 1922, and it is estimated that acid to the extent of some 17,000–18,000 tons of 100% H_2SO_4 will have been produced from this source during the year. Increase in the production of acid from calcination of zinc ores in this country has been slow, largely due to difficulties experienced in providing suitable mechanical calciners, but considerable experimental work has been carried out, and before long results should indicate that difficulties are being overcome ; meanwhile improved results have been attained with hand calciners.

A newly-discovered large deposit of sulphur is reported from Texas,[68] and should be producing during the coming year, so that ample world supplies of this material are at present assured.

J. W. Parkes[69] gives a valuable technical record of the construction and working of the Kynoch oleum plants during the war. These plants were of the Mannheim type fed by gases from pyrites burners, both mechanical, and of the kiln type ; full details are given of cooling, draughting, absorption, and conversion. Conversion in this case was effected in two stages, firstly in a contact shaft containing burnt lump pyrites, and secondly the purified residual SO_2 is passed through heated platinised mats. At the present time it does not seem probable that developments on the lines of Mannheim plant are likely to occur, the indications being that, with the perfection of electrostatic methods for gas purification, future developments in oleum plant will be in the direction of single contact conversion.

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[68] *J.*, 1922, 79R.

[69] *J.*, 1922, 100T.

F. D. Miles and W. Sarginson[70] give data on the occurrence and effect of fluctuating combustion in the sulphur burners of the Grillo oleum plant at Gretna. These burners, which were of the flat tray type, were charged by hand, and the authors consider fluctuations are inevitable in either sulphur or pyrites burners where hand charging is practised. Conversion efficiencies were found to vary with the variations in concentration of the gases, and experiments showed that a rapid increase in concentration led to a fall in the conversion efficiency of the top layer of the contact mass, thus throwing an extra load on to the succeeding layers. Rapidity of catalysis increases with temperature, but if the temperature of the top tray was increased to obtain a greater conversion at that point, the whole converter became so hot that total efficiencies fell away owing to the less complete conversion at the higher temperatures attained in succeeding layers. It is suggested therefore that the Grillo type of converter is at a disadvantage in this respect as compared with types where conversion takes place independently in two or possibly more sections, owing to the fact that the trays in the Grillo converter are thermally dependent on one another; high temperature for speed of conversion, and lower temperature for most complete conversion, are incompatible in one thermal unit.

In No. 5 of the Technical Records of Explosives Supply, 1915–1918,[71] are given very complete details of the operation of the oleum plants at the Government factories during the war. The title, "Manufacture of Sulphuric Acid by the Contact Process," is well merited by its contents, and it is a record which should be carefully studied by all who are interested in the manufacture of contact acid.

T. F. Banigan[72] refers to the fact that cast-iron pipes and malleable castings, after long exposure to sulphur trioxide, frequently crack suddenly, although no corrosion can be detected previously. Although silicon carbide is unaffected by oleum, it is shown experimentally that amorphous silicon or silicon alloyed with iron is rapidly oxidised by 15% oleum, and the failures above referred to are probably due to oxidation of silicon particles within the casting giving rise to internal strains.

[70] *J.*, 1922, 183T.
[71] *J.*, 1922, 378R.
[72] *J. Ind. Eng. Chem.*, 1922, **14**, 323; *J.*, 1922, 411A

GLASS.

By Morris W. Travers, D.Sc., F.R.S.

In estimating progress in scientific investigation in the glass industry, reference must be made to the fact that a very large amount of public money is being spent annually on technical research, the results of which are neither available for information, nor subject to criticism. Research on glass is being carried out by the National Physical Laboratory, the Department of Chemical Inspection, Woolwich Arsenal, the Glass Research Association, and the British Scientific Instrument Research Association; and while the expenditure from the public funds cannot be less than £20,000 per annum, very little information is available as to the results obtained.

The Society of Glass Technology continues to flourish, and its journal, under the editorship of Professor W. E. S. Turner, President of the Society for this year, continues to be the leading journal connected with the industry. The three quarterly numbers which have been issued during 1922 show that there is no diminution in the output of scientific work from the Department of Glass Technology in the University of Sheffield, though there appears to be a distinct diminution in the number of papers contributed to the journal from other sources. It is to be hoped that the interest taken in glass technology by scientific workers, and by workers in allied industries, is not really diminishing. The number of abstracts is maintained, and a study of these reveals the interesting fact that, so scattered is information relating to glass, the first fifty-one abstracts of papers on the manufacture and properties of glass ar drawn from twenty-six different journals. This fact gives measure of the value of these abstracts to those interested in th industry. The Journal of the American Ceramic Society, of which Glass Section was recently formed, contains very few papers connected with the science and technology of glass manufacture Progress on the technical side of the industry in America must b estimated from the study of patent literature, and from suc journals as the *National Glass Budget*, or the *Glass Container.* vast amount of scientific work in connexion with the behaviour o glasses is still, and will continue to be, carried out in the Geophysica Laboratory at Washington, and it is fortunate for the industry tha its fundamental problems are identical with those of geophysics and receive the attention of this institution.

Professor Turner's presidential address to the Society of Glass Technology consists of a survey of the history of the glass industry from the earliest times down to the present day. Opening with a critical discussion on modern discoveries bearing on the early history of glass-making in this country, he proceeds to trace the development, and often the decline, of glass-making in various centres. Glass-making appears to have been established as an industry in this country late in the sixteenth century, and at the end of the seventeenth century there were as many as eighty-eight glass-houses in England. Then followed a period of stagnation; but between the years 1833 and 1874 the industry, in spite of excise restrictions, shared in the general industrial prosperity, and the number of glass houses in the United Kingdom increased from 126 to 240. Then followed a decline. Professor Turner's account of the operation and effects of the excise regulations is most instructive; and it seems almost incredible that the industry could have survived at all under regulations which compelled the manufacturer to fill his pots under the eye of an inspector, and to anneal the glass in locked kilns. The repeal of the duties in 1845, which relieved the industries of taxation amounting to £845,000, and of intolerable control, gave a great impetus to development, which reached a climax in 1874.

The paper contains statistical tables relating to imports, exports, etc. Dealing with the fifteen years prior to the war, the value of the imports appears to have remained almost constant, while the exports increased from £885,000 to £1,814,000. At the same time the number of factories at work, and of men employed in the industry, showed some slight diminution. Allowing for improved methods of production, it is probable that the output did not materially increase or decrease during the period, and that the increased value of the exports represents in part increase in prices, and in part a shifting of the industry from home to export trade. It is clear, however, that the industry was not developing, or modifying its methods to meet the demands for new types of goods, which were being sent in from abroad. As Professor Turner shows, many new ideas, such as that of producing bottles by machinery, had their origin in British glass houses, but were actually developed and applied to large-scale production by American engineers.

THE NATURE OF GLASS.

The formation of glasses involves the freezing of equilibria, established at temperatures at which they are more or less mobile, so that in glasses at ordinary temperatures we have systems the nature of which may be materially dependent on their previous history. As a mass of glass cools, a temperature gradient, and therefore a density gradient is established in it, and when the mass is at uniform temperature stresses are set up in it, the magnitude and character of which depend upon the steepness of the temperature gradient during cooling, and the form of the mass. The problems relating to glass are complicated by the fact that there is great difficulty in securing homogeneity in melts.

We have no definite knowledge indicating whether glass is a homogeneous solution, or of the nature of a colloid, but we do know from recent researches that the transition from the mobile to the rigid condition is not a continuous one, though the transition is not sharp, as in the case of that between crystalline solids and liquids. Lebedeff[1] suggests that the abnormal expansion of glasses below their softening point is connected with the $\alpha\text{-} \rightleftarrows \beta$-quartz change, which also takes place a little below 600° C. This is probably a coincidence, since abnormal expansion below the softening point is a property of boric oxide glass, of the glasses of organic substances, and possibly of gels. Information as to the nature of glass will probably result from the researches on the stress-optical phenomena, such as are now being carried out by Filon, Adams and Williamson, Twyman, and others.

Information as to the relationship between the physical and chemical properties of glasses and their chemical composition is of immediate importance to the practical glass manufacturer, and will ultimately be of use to scientific investigators, though it is too much to expect that simple relationships between properties will be found to be of wide application. However, the application of additive formulæ to groups of glasses is useful. In this connexion S. English and W. E. S. Turner[2] have continued their researches on the relation between composition and density, investigating the soda-lime-magnesia glasses.

ANNEALING.

Few references to annealing problems appear in the literature issued during the year. F. Twyman, who first attacked the problem of scientific annealing of glassware, has designed an apparatus for controlling the process of annealing without the use of a pyrometer.[3] In this instrument a rod of the glass to be annealed is subjected to a definite stress and the instrument itself is placed in the lehr amongst the goods to be annealed. The tilting of a pointer indicates when the original stress has fallen to a definite lower value, so that the interval between placing the instrument in the lehr and the moment at which the pointer begins to tilt, measures the time required for stresses in the glass to fall to a certain fraction of the initial stress, or the time of relaxation of the stress, which may be assumed to be the maximum existing in the freshly-made goods, to a limit which may be considered negligible. This is the annealing time under the conditions of temperature which actually prevail at the level in the lehr at which the goods are being annealed. Since there is always a steep temperature gradient between the top and bottom of a lehr, the instrument gives a more accurate indication as to whether proper temperature conditions prevail in it than can a pyrometer placed in the crown.

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[1] *Trans. Opt. Soc. Petrograd*, 1921, **2**, No. 10.

[2] *J. Soc. Glass Tech.*, 1922, **6**, 228.

[3] *Ibid.*, 1922, **6**, 45.

E. D. Williamson[4] contributes from the Geophysical Laboratory a further note on the application of the theory of annealing developed by Adams and himself. From the equations representing the results of experimental work previously described, the most favourable conditions for annealing a given piece of glass can be deduced. Formulæ are found which, used in conjunction with tables of the elastic and annealing constants of the glass, show at what temperature to hold the glass, how long to hold it at that temperature, and how rapidly to cool it in order to get any degree of fineness of annealing in the least possible time. Examples are solved to illustrate the process.

CHEMICAL CHANGES DURING THE MELTING OF GLASS.

Papers on the dissociation of ferric and manganic oxides in glass are published by J. C. Hostetter and H. S. Roberts,[5] and by E. N. Bunting.[6] The ratio ferric oxide-ferrous oxide depends upon the concentration of the iron, the composition of the glass, and the temperature, and some glasses lose oxygen during the fining process, and re-absorb oxygen at working temperatures. This may account for the change in the colour and transparency of some optical glasses after long stirring. Similar changes take place in the case of manganese. Oxygen is given off in quantity as the glass is melted at 1400° *in vacuo*. It is well known that if a pot of glass, containing manganese, is allowed to stand for a long time in a semi-fluid condition, the glass tends to become pink. This was observed in some works during the late coal strike.

A general discussion on the melting of glass was opened at a meeting of the Society of Glass Technology, on November 16th, 1921, and was continued on February 15th, 1922.[7] A large number of practical and scientific questions were discussed, and those interested in the subject should read the reports of the meetings. In a paper by F. W. Adams[8] the manufacture of bottles and containers of colourless glass, using selenium, is discussed in the light of practical experience.

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[4] *J. Washington Acad. Sci.*, 1922, **12**, 1; *J.*, 1922, 176A

[5] Geophysical Laboratory, "Optical Glass," No. 39; *cf. J.*, 1922, 100A.

[6] *J. Amer. Ceram. Soc.*, 1922, **5**, 594.

[7] *J. Soc. Glass Tech.*, 1922, **6**.

[8] *Ibid.*, 1922, **6**, 205.

NEW TYPES OF GLASS.

Reference has been made[9] to a new type of chemical glassware which has appeared on the British market, but information as to its composition and properties is not available.

THE DURABILITY OF GLASS.

The attack of glass surfaces by water and by chemical reagents is a subject of perennial controversy, and the year has seen the publication of several papers dealing with it. G. W. Morey[10] discusses the solubility and decomposition of complex systems generally, from the standpoint of the phase rule, and as a particular case that of the system $H_2O—K_2SiO_3—K_2O$. This system has been studied over a range of temperature between 200° and 1000° C., and the results indicate that potassium silicate solutions have no stable existence at ordinary temperatures. Under these conditions true equilibrium in any mixture of $H_2O—SiO_2—K_2O$ would mean a solution containing a vanishingly small quantity of silica, in equilibrium with a solid crystalline phase of pure silica. Potash water-glass solutions which contain large amounts of colloidal silica bear no known relation to the solutions which would exist in equilibrium with crystalline phases.

This system is analogous to the complex systems consisting of glasses and water, in which the aqueous phase is an alkaline liquid containing traces of such oxides as B_2O_3. The material dissolved is the product of the decomposition of the glass, and such silica as is removed from the glass passes into the aqueous phase as colloid; but under no condition does the composition of the aqueous phase give a measure of the solubility of the glass. The term "solubility" should not be applied to the phenomenon.

The mechanism of the attack of glasses by water or reagents seems first to involve the decomposition of the silicate in the surface layers, with removal of the alkali, leaving a layer of silica or silicious material. This may suffer mechanical disintegration, passing into the aqueous phase, either in the colloidal condition, or in microscopic flakes. The rate of removal of colloidal material depends upon the peptising action of the solution in contact with the glass, which may explain the distinctive action of the same reagent in different concentrations. The formation of flakes may be due to the inhomogeneity of the glass itself. If the residue left after the removal of the alkali did not pass into the aqueous phase in the colloidal condition it would be likely to become detached in flakes. The attack of glassware by reagents is, then, a combination of chemical and mechanical processes, and it is not astonishing that attempts to connect the rate of chemical attack with the chemical properties of glasses have not led to definite conclusions.

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[9] *Nature*, Dec. 23, 1922.

[10] Geophysical Laboratory.

The physical properties of glass are, as is well known, materially dependent upon its previous history. The nature of the surface depends upon whether the glass is newly worked and allowed to cool without being touched,[11] worked in the ordinary manner, fractured, ground or polished with various abrasives, weathered, or fire-polished after previous treatment. Griffith's experiments point to very marked differences in the nature of a thin rod of glass, drawn out in the flame and cooled without contact with other material, when its tenacity is very much greater than after it has been touched with the fingers. His explanation that the change is due to molecular rearrangement, and the development of surface flaws of dimensions comparable with molecular distances, appears to be justified. For obvious reasons the investigation of chemical attack on such surfaces by water presents insuperable difficulties. The attack of optical glass surfaces after varying treatment has been the subject of an investigation by the British Scientific Instrument Research Association.[12] The method of investigation involved the measurement of the alkalinity of the surface by a modification of the iodoeosin method, which was very carefully studied. The results are expressed in terms of iodoeosin absorbed per square decimetre of surface, and the values divided by 13·48 give the equivalents in terms of Na_2O liberated. Iodoeosin values were obtained for a series of optical glasses, under the following conditions :—

Column 1. Glass fractured under iodoeosin solution.
Column 2. Glass freshly fractured.
Column 3. Weathered fracture.
Column 4. Freshly-polished surface.
Column 5. Polished surface weathered for seven days.
Column 6. Polished and heated to 150° for four hours.

The following results were obtained in the case of the first ten glasses in the list :—

No.	Glass.	1.	2.	3.	4.	5.	6.
1	Fluor Crown	0·03	0·03	0·02	0·02	0·02	0·03
2	Boro-silicate Crown	0·10	0·11	0·07	0·02	0·03	0·04
3	Boro-silicate Crown	0·08	0·08	0·03	0·03	0·03	0·04
4	Boro-silicate Crown	0·17	0·17	0·08	0·02	0·02	0·03
5	Hard Crown	0·18	0·16	0·07	0·04	0·06	0·04
6	Soft Crown	0·33	0·19	0·69	0·08	0·26	0·23
7	Light Barium Crown	0·16	0·14	0·05	0·03	0·02	0·03
8	Medium Barium Crown	0·12	0·08	0·03	0·04	0·04	0·03
9	Dense Barium Crown	0·22	0·21	0·08	0·04	0·03	0·03
10	Dense Barium Crown	0·21	0·19	0·06	0·03	0·03	0·03

[11] Griffith, *Phil. Trans.*, 1920.

[12] *Report*, 1921.

Except in the case of No. 6, which seems to be an exceptional glass, it may be considered doubtful whether the results in columns 1 and 2 represent any real difference in the properties of the surface of the glass immediately after fracture, and a few moments later. It is evident, however, that the result of polishing is to reduce the iodoeosin factor for all glasses to a value which varies between narrow limits. The results in columns 4, 5 and 6 are, with the exception of those relating to glasses Nos. 5 and 6, expressed as a single significant figure between the extreme limits 2 and 4. They can, therefore, only be taken as indicating the direction in which the properties tend to change after treatment. It would appear from the results that the effect of polishing is to increase the resistance of glasses to attack by moisture, and that, with certain exceptions, polished glasses differ very little amongst themselves in their behaviour under the iodoeosin test. It would be interesting to know how far the results of this test coincide with practical experience as to the durability of the glasses.

Reference may be made to the observation of Preston[19] that the rate of attack of a polished surface by hydrofluoric acid hardly diminishes at all after the removal by solution of the polished layer.[13]

Professor Turner and the staff of the Department of Glass Technology at Sheffield[14] are continuing their experimental investigations on the relationship between the chemical composition of glasses and attack by reagents. Comparing the lime-soda and magnesia-soda glasses, they find that on substituting lime by magnesia up to about 3·5 mols. % the resistance of the glass to attack by hydrochloric acid is increased, but for higher $M''O$ content the lime glasses were the more resistant. Magnesia glasses are generally more resistant than lime glasses to attack by water, and less resistant to attack by alkalis. These results have an important bearing on the use of magnesian limestone in the glass industry.

W. L. Baillie[15] has published an important paper on the application of Zulkowski's theory of the relationship between composition and resistance to chemical attack. In its simplest form, Zulkowski's theory may be stated as follows. In glasses of the type $mR_2O,nRO,xSiO_2$, the difference $mR_2O - nRO$ represents the molecular excess of either oxide, present as a simple silicate, the oxide present in lowest molecular concentration being supposed to be in combination as a double silicate of the form $(R_2O,RO),ySiO_2$. The "solubility" of the glass was supposed by Zulkowski to be proportional to the numerical magnitude of the molecular excess of the simple silicate. In the case of the simple soda lime glasses those of the general form $R_2O,RO,xSiO_2$ should be the most highly resistant to chemical attack, and those containing molecular excess of either lime or soda should be less resistant. As a matter of fact the rate of chemical attack by water of simple glasses of the form $mR_2O,nRO,xSiO_2$ increases rapidly with molecular excess of alkali, but not with molecular excess of lime. However, glasses containing large quantities of $R''O$ oxides are uncommon, and of little practical importance.

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[13] *Trans. Opt. Soc.*, **23**, 154.

[14] *J. Soc. Glass Tech.*, 1922, **6**, 11, 30.

[15] *Ibid.*, 1922, **6**, 68.

Many important technical glasses contain Al_2O_3 or B_2O_3, or both of these oxides, which, in a general way, increase the resistance of the glasses to chemical attack, neutralising the effect of basic excess as defined by Zulkowski. Baillie therefore assumes that, when the sesquioxides are present, there exist in the glass besides double and single silicates, complex silicates, which he assumes to have the general form, $3MO,(B,Al)_2O_3,xSiO_2$, where M is equivalent of one of the bases. On this assumption he calculates from the composition of each glass a quantity which represents the basic excess, and which he terms the "reactivity coefficient."

The paper contains a review and summary of the results obtained by a large number of workers for the rate of chemical attack on series of glasses of known composition. For these Baillie calculates the value of the reactivity coefficient, and he finds that the order in which the glasses are arranged as the result of the calculations, is in general agreement with the results of experimental investigations. Small or negative values of the reactivity coefficient are generally associated with highly resistant glasses, while glasses for which the value is large are unsuitable for the manufacture of scientific instruments, or for similar uses.

Special methods of testing glasses for particular purposes are recommended by various authorities. The methods suggested by the National Physical Laboratory, the Institute of Chemistry, Prof. Turner of the University of Sheffield, the American Bureau of Standards, and Dr. Peddle, of the Derby Crown Glass Company, and others have already been published. The British Scientific Instrument Research Association (*loc. cit.*) have developed and improved the well known iodoeosin test for the alkalinity of glassware.

W. E. S. Turner[16] reviews at some length the methods which have been applied to the testing of scientific and utility glassware, calling attention to the fact that each investigator has, as a rule, used one method only, and that the results obtained by different observers are not comparable, though Peddle's qualitative tests of the degree of attack of polished glass surfaces exposed to the atmosphere agreed with the results obtained by treating the powdered glasses with water. He considers that in the case of chemical apparatus the test should be carried out on a piece of glass cut from the apparatus, which would eliminate the difficulty arising from attempts to compare results obtained, for example, with large and small flasks or beakers. As an alternative he proposes testing glasses in the form of powder, sieved between limits, and suspended in a platinum basket.

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[16] *Ibid.*, 1922, **6**, 30.

W. L. Baillie and F. E. Wilson[17] advocate the use of the autoclave test as a general method for determining the suitability of glass for the manufacture of instruments. While applicable to the more resistant glasses it seems too drastic for application to the softer glasses, which are used for the manufacture of delicate apparatus. Special methods for the testing of utility glassware are suggested by several authors, and reference to the papers will be found in the Abstracts of the Society of Glass Technology.

At a meeting of the Society of Glass Technology, held in London on December 13th, the testing of glassware formed the subject of a general discussion. The discussion was introduced by papers read by W. L. Baillie, by W. H. Withey (National Physical Laboratory), and by W. E. S. Turner. Baillie emphasised the importance of using a single reagent for testing glassware, and stated that his experiments led to the conclusion that the action of steam alone in the autoclave gave a reliable indication of the durability of a glass. The measure of durability was the alkali set free under specified conditions, and it was only necessary to define the duration of the test, the pressure to be maintained in the autoclave, and the limiting amount of alkali per unit of surface, in excess of which a glass could not be considered suitable for a particular purpose.

Withey admitted that the autoclave tests for such articles as water gauge tubes was open to no objection. Experiments carried out at the National Physical Laboratory showed, however, that in the case of resistance glasses, in which it was necessary to use a high pressure in the autoclave, and to subject the glass to conditions which must be fixed arbitrarily, and which had no relation to laboratory practice, misleading results were often obtained. From these experiments it appeared that the autoclave test was only reliable when applied at different pressures, and for short intervals of time. This introduced complications, and made it difficult to interpret the results obtained with a series of glasses, and to classify them in the order of their durability. The conclusion arrived at by the National Physical Laboratory appears to be entirely in conflict with that put forward by the Directorate of Chemical Inspection, Woolwich.

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[17] *J.*, 1922, 45T.

Turner thought that the autoclave test was not, in itself, a criterion of the durability of a glass. He cited the case of a glass of the composition SiO_2 76%, CaO 6–7%, Na_2O 11%, K_2O 5–6%, which withstood the action of boiling water or steam at 100° as well as, or better than, most resistance glasses, but which went to pieces in the autoclave. He believed that if a general test were to be adopted it would be that of treating powdered glass, sieved between certain limits, with boiling water.

In the discussion M. W. Travers agreed with Turner's suggestion as to a rough test for general purposes. For particular purposes it would be necessary to subject the glass to identical treatment to that which it would receive when in use. For an analytical operation, using a particular reagent for two hours, the glass might be tested by treating it with the same reagent, under the same conditions, for, say, eight hours. If a material quantity of the substance of the glass passed into solution, the glass should be rejected, or a correction made for the error introduced, if this were possible. An analyst would be very unwise to rely on any test involving the action of water on glass as indicating its resistance to acids.

It would seem that a very large amount of time and money have been devoted to the attempt to discover a single test for the durability of glassware. Practically speaking, we do not seem to be near to the solution of the problem, and theory would suggest that it is insoluble. From the point of view of the analyst the problem is not, in its essentials, a very complicated one. A few forms of apparatus, particularly those used in bacteriological work, must be subjected to the action of water and steam under slight pressure. There is no difficulty in specifying the conditions of a suitable test. Other forms of apparatus have to withstand the action of moderately dilute analytical reagents for a limited time. Again, tests can easily be prescribed suited to apparatus of widely varying dimensions. Finally, it may be well to specify tests for the resistance of glass and porcelain vessels to strong acids; but those who would use strong acids in glass apparatus would be wise to make use of the special acid resisting glasses which are on the market, and those who use strongly alkaline liquids in glass apparatus must expect to find the constituents of the glass in their solutions.

OPTICAL GLASS.

During the two years previous to the year 1922, technical and scientific literature was rich in papers relating to the manufacture of optical glass. During the past year the amount of original work which has been published is almost negligible, and it would appear that the interest in this subject, awakened by the war, is now declining. C. J. Peddle[18] publishes an account of his work in connexion with the development of the industry during the war. Prior to 1914 about 60% of the optical glass used in this country was imported from Germany. At the outbreak of war only Messrs. Chance Bros. were actually engaged in the manufacture of optical glass in Great Britain. In June, 1914, Messrs. Wood Bros. began to manufacture optical glass, and before the end of the war the Derby Crown Glass Co., under the technical direction of Dr. Peddle, was able to place seventy varieties of optical glass at the service of instrument makers. About one hundred varieties of glass were made at Derby. The paper contains a summary of the work on the relationship between the properties and composition of glasses, which has formed the subject of a series of papers in the *Journal of the Society of Glass Technology*, and also an account of the processes of melting and working optical glasses. It is to be regretted that Dr. Peddle is no longer connected with the glass industry.

GRINDING AND POLISHING.

The Optical Society has published a series of papers which form a valuable contribution to our knowledge of the phenomena connected with the cutting, grinding, and polishing of glass.[19]

It has commonly been supposed that a grain of abrasive, in the process of grinding a brittle material, acts by cutting or pushing away the material which obstructs its passage, either flaking out conchoidal splinters, or by shearing off the tops of existing prominences. Abrasive materials may act in this way to a certain and limited extent; but it is now shown that the removal of material in the main is the result of a totally different process.

Preston's paper opens with an account of an experimental investigation into the action of a hard surface of limited area, such as a needle point, a steel ball, or the curved cutting edge of a glazier's diamond, upon the surface of a piece of glass. He demonstrates, by means of admirable illustrations, that the result is to produce flaws or cracks in the surface. In the case of the glazier's diamond, material is actually removed at the surface as the tool advances, and the more so if a point instead of the curved edge bears on the glass. The flaws produced by pressure penetrate far below the bottom of the scratch, particularly when the proper edge of the diamond is used. The production of deep flaws is material, and that of the visible scratch is immaterial to the "cutting" of the glass. In the case of a rolling ball the track consists of a series of arcuate flaws or fractures with their concave surfaces facing in the direction from which the ball travels. Under heavy pressure the flaws tend to curl round and approach the surface, while longitudinal flaws develop parallel to the median line.

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[18] *Trans. Opt. Soc.*, 1921-22, **23**, 103.

[19] "The Structure of Abraded Glass Surfaces," F. W. Preston, ***Trans. Opt. Soc.***, **23**, 141; "The Stress Condition surrounding a Diamond Cut in Glass," A. J. Dalladay, *ibid.*, p. 165; "Some Measurements of Stresses produced at Surfaces of Glass by Grinding with Loose Abrasives," A. J. Dalladay, *ibid.*, p. 170.

In these two cases the result of the action of the tool is to produce flaws in the glass surface, without, *of necessity*, removing material from it. When a number of tracks such as are made by a single steel ball, or other hard surface, intersect, the flaws also intersect, and material begins to be detached from the surface. When a loose abrasive is used under an iron tool the track of every grain of the abrasive which is pressed between the tool and the glass is a series of flaws, and where the flaws which constitute separate tracks intersect suitably, material is removed.

This theory is supported by the well-known discovery by F. Twyman, that a "greyed" surface of glass is under stress, the actual surface being in compression and the glass just below the surface in tension. This is due to the wedging of minute particles of glass into the flaws produced by the abrasive. When the wedged particles are removed by the action of acid, or by polishing, the stress disappears. The stress set up in a diamond cut is produced in a similar manner.

The essential character of a surface which has been "greyed" or reduced to the limit of smoothness by a fine abrasive under a metal tool is that not merely does it consist of hills and hollows, but that beneath those hills and hollows are flaws which extend to two or three times their depth downward into the glass.

Study of the rate of attack of "greyed" and polished surfaces by hydrofluoric acid shows that the rate of solution of the greyed surface diminishes rapidly with time, while the rate of solution of the polished surface hardly diminishes at all. The rate of attack in both cases becomes ultimately identical.

Preston attributes the polishing of glass by a fine abrasive under a tool covered with pitch or felt to phenomena identical with those already described. A fine flaw complex is first produced, which, in the final stage of dry polishing, is actually "broken away by the roots." At the same time a very slight molecular flowing of the surface (Beilby effect) results in the covering of the last traces of the flaw complex produced in the greying process. This view is supported by experiments in the etching of polished surfaces.

MECHANICAL METHODS OF WORKING GLASS.

Numerous patents relating to improvements in the method of feeding glass to machines for the formation of bottles etc. have been published during the year, but none of them involves any new principle, nor can they be described without reference to diagrams.

Abstracts of patent specifications, with diagrams, are published in the *Journal of the Society of Glass Technology.*

Mechanical methods of drawing sheet glass have, during the past few years, been successfully operated by the Libby-Owens process in America and by the Fourcault process in Belgium, and a large factory for the operation of the latter process has recently been constructed in this country. In the Fourcault process the glass while in the plastic condition does not pass over rollers, or come into contact with any other surface, so that, when it is successfully operated, a very beautiful finish is obtained, which is said to be equal to that of polished plate. Patent literature indicates that inventors are busy attempting to develop other methods of manufacturing sheet glass mechanically. J. Cox[20] describes a method of feeding glass between rollers which are heated to 900°, and which, in consequence, become covered with a layer of glass. J. P. Crowley and others[21] describe a method in which the molten glass is fed between rollers coated with a layer of molten lead or tin to prevent the adhesion of the glass. As to whether these methods have been tested is unknown.

The mechanical production of glass tubing is also a matter of considerable interest to inventors. Philips' Gloeilampenfabriek (Holland)[22] describes a process which differs only from the well-known Libby-Owens process in that the molten glass is fed on to the inside instead of on to the outside of a revolving cone. The Libby-Owens process is now being operated in this country.

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[20] E.P. 175,044.

[21] U.S.P. 1,422,036.

[22] E.P. 172,289.

arcuate flaws or fractures with their concave surfaces facing in the direction from which the ball travels. Under heavy pressure the flaws tend to curl round and approach the surface, while longitudinal flaws develop parallel to the median line.

In these two cases the result of the action of the tool is to produce flaws in the glass surface, without, *of necessity,* removing material from it. When a number of tracks such as are made by a single steel ball, or other hard surface, intersect, the flaws also intersect, and material begins to be detached from the surface. When a loose abrasive is used under an iron tool the track of every grain of the abrasive which is pressed between the tool and the glass is a series of flaws, and where the flaws which constitute separate tracks intersect suitably, material is removed.

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pyrites invariably remained in the clay. In many respects his results corroborate the conclusions previously arrived at by Bleininger (*cf. Trans. Amer. Ceram. Soc.*, 1913, **15**, 43). It cannot reasonably be doubted that the verdict pronounced by Kohl and other unbiassed observers represents the true position; and the fact that the method of purifying clays by this process has not made greater progress since its inauguration may, perhaps, be taken as further corroborative evidence of its shortcomings. Nevertheless, its introduction has had a salutary effect, if only in disclosing the possibilities of sedimentation with slips containing various electrolytes.

Earlier work on the action of bacteria on clays is recalled by a contribution by W. J. Vernadsky,[3] who confirms previous observations, namely, that bacterial action increases the proportion of free hydrates of alumina in a clay. As is well known, this action accounts, at least partially, for the "weathering" or "ageing" process to which most clays are submitted. But a few years ago the writer of this review saw an experiment conducted in which a special body was inoculated with selected bacteria for the express purpose of increasing the plasticity.

The difficulty of interpreting the nature and behaviour of the clay molecule has given to us many hypotheses, some based on little experience and indefinite experiment. Accurate study of this complex problem is always welcome, and for this reason the work of H. S. Houldsworth and J. W. Cobb[4] on "The Behaviour of Fireclays, Bauxite, etc., on Heating" is to be commended. By the application of the Roberts-Austen method of determining transition points, they have obtained, with fireclay, valuable data relating to the two endothermic changes taking place at about 100° and 520° C. respectively and the exothermic change at about 930° C. Although the authors draw no conclusions from the results, it may be noted that Mellor's conception of the behaviour of the kaolinite molecule is in no way refuted by this work. C. E. Moore[5] has also attempted the elucidation of this problem from a somewhat different standpoint. He has studied the variation, caused by heating, in the contraction, porosity, specific gravity, hygroscopicity, and solubility in acid of Stourbridge fireclays. Supplementing these data, he has investigated "dehydration" and "heating curve" phenomena. The results must be of much value to the Stourbridge manufacturer. The author, however, with a decided suggestion of dogmatism, has adopted a conception of the clay molecule based on the hexite-pentite theory of Asch. Owing to the highly controversial nature of the subject, criticism of this theory is of doubtful value; however, it is pointed out that in ceramics its utility has long disappeared, owing, it is suggested, to the increasing influence of the "phase-rule" implications.

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[3] *Comptes rend.*, 1922, **175**, 450.
[4] *J.*, 1922, 447R.
[5] *Ibid.*

Although seven different crystalline modifications of silica are definitely known, there remain two forms of this oxide of unknown constitution. These, comprising flint and chalcedony, have generally been described as "cryptocrystalline," though Fenner has already suggested that chalcedony is probably a form of quartz. E. W. Washburn and L. Navias[6] have made an exhaustive examination of these minerals and have shown beyond doubt that they contain large proportions of crystalline quartz. The X-ray spectra of each is identical with that of quartz, while such physical properties as specific gravity, index of refraction, and coefficient of thermal expansion are comparable with those of the latter mineral. By the same means these authors have demonstrated that the product of calcination of both flint and chalcedony is mainly cristobalite.

Details relating to the manufacture of dolomite earthenware are published by G. Steinbrecht.[7] In his interesting contribution, this writer not only points out the various difficulties experienced in manufacturing, but also gives some useful hints on the best methods of overcoming them. Some years ago Cannan conducted extensive research work on the use of dolomite as a body flux, but hitherto no operations on a large scale have resulted therefrom. Enormous supplies of the material are available in Great Britain, and there appears to be no reason why an attempt should not be made to incorporate it in bodies of an inferior type.

The actual making of large ceramic objects is an operation which comparatively seldom forms the subject of systematic observation and detailed record, yet during the period under review two such contributions have appeared in the same publication. J. Clark[8] and T. A. Klinefelter and F. C. Parsons[9] have dealt with the subject of "pressing" in a comprehensive manner, and their contributions, which are well illustrated, will doubtless focus attention on the methods adopted at different works. Moreover, it may confidently be expected that more or less criticism will be forthcoming, since the predominant factor in all such practical operations is undoubtedly the personal element.

The excessive losses which are experienced periodically in pottery manufacture could be curtailed by a more complete understanding of the fundamental principles underlying the various processes. Particularly is this the case with crooked ware, for our knowledge of the causes of this trouble is for the most part empirical and very incomplete. For this reason the contribution by C. H. Lees[10] is to be welcomed, inasmuch as the author deals with principles in a manner totally new to the industry. Despite the fact that his contribution is of a purely theoretical nature, his data are of considerable importance from a practical point of view, since the heavy monetary losses incurred from crooked ware could be considerably reduced by the application of the principles enunciated by this author.

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[6] *J. Amer. Ceram. Soc.*, 1922, **5**, 565.

[7] *Keram. Rund.*, 1922, **30**, 471.

[8] *J. Amer. Ceram. Soc.*, 1922, **5**, 623.

[9] *Ibid.*, 1922, **5**, 632.

Many interesting and controversial points are referred to by C. N. White[11] in his dissertation on chemical porcelain. This product is a heterogeneous compound, and consequently the laws relating to ideal solid solutions require modification before they can be applied. The author suggests that the higher the proportion of crystallinity produced during firing, compared with the possible degree of crystalline structure, the better will the product withstand rapid thermal changes; he claims that stability is really a function of the sillimanite formed.

These observations are worthy of note, for it has been pointed out previously by many investigators, notably by Mellor, that the deterioration of porcelain pyrometer tubes, refractory saggars, etc., is largely due to the formation of sillimanite whilst in use.

As is suggested by C. W. Hill[12] in a recent publication, the field for research in ceramics is practically unlimited. As a type of problem requiring elucidation, he mentions the rejuvenation of old plaster moulds. Theoretically, he maintains, there ought to be no difficulty about the process. It is evident that the author has heard of the many unsuccessful attempts which have been made to solve this problem, since he points out that the presence of a high percentage of anhydrous sulphate may be detrimental to the process. One may be permitted to draw attention also to the fact that other side issues, such as the presence of sodium sulphate and calcium silicate in moulds used for casting with alkaline slip, render the problem still more interesting and complicated.

S. B. Larkin[13] suggests that equal parts of cement and plaster would make an ideal mixture for mould-makers' cases. Unfortunately, no specific type of cement is mentioned. It may be noted, however, that mixtures incorporating "Keene's" cement have been used in moulds for cup handles and would probably be of service in the manner suggested.

Lack of fundamental data relating to the "clay flow" in expression machines has been responsible, at various times, for abnormal losses in certain branches of the ceramic industry. The trouble is accentuated by the fact that in some cases the lamination only develops after the goods have been put into service. This is particularly the case with certain types of machine-made roofing tiles. For this reason J. J. F. Brand's[14] contribution to the literature of the subject is to be welcomed. It contains many valuable data and the suggestions put forward should not be difficult of application. The fact that the effect of varying the water distribution within the mass is dealt with at some length should add further interest to the paper.

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[10] *J.*, 1922, 446R.

[11] *Trans. Ceram. Soc.*, 1922, **21**, 320.

[12] *J. Amer. Ceram Soc.*, 1922, **5**, 732.

[13] *Brick and Clay Record*, 1922, **61**, 255.

The degree of precision demanded in ceramic fittings to be used in certain branches of the electrical industry, renders it imperative that each article should conform closely to required standards. In practice it has been shown that attention to the ordinary routine is not sufficient, and any research that will assist in effecting still more rigid application of sound principles will be welcomed by the trade in general. Data supplied by H. Spurrier[15] in a paper on dust-press practice are of great value in this connexion. In his experiments he endeavoured to find out the flow of the dust in the dies while the pressure was being exerted ; he shows that there are stream or flow lines within the dust, and he suggests that, in order to overcome the defects arising from these movements, a special study is necessary with a view to determine the best method of filling the mould.

A successful attempt has been made by I. E. Sproat[16] to correlate data regarding the type of body, mechanical strength when dry, and the various defects which become apparent after biscuit firing. The conclusions arrived at by the author indicate that the proportion of cracked, crooked, or strained ware can be regulated largely by modifications of the recipe. The data supplied certainly merit careful attention from manufacturers of whiteware. The need of such information as is given in this paper has, in fact, been referred to repeatedly in ceramic literature. Furthermore, great benefit would be derived from an extension of these investigations to include variations in the body materials as distinct from alteration of recipes.

Further data relating to the possibilities of mechanical handling in ceramic works are recorded in a contribution by A. P. Ball.[17] The diagrams accompanying the paper clearly show that in the plant under review principles have been followed which have proved successful in engineering practice. It is also to be noted that the equipment would require modification if used on whiteware factories, since the large amount of iron used in its construction (unless this be kept well painted etc.) would not be conducive to cleanliness.

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[14] *J. Amer. Ceram. Soc.*, 1922, **5**, 355.

[15] *Ibid.*, 1922, **5**, 798.

[16] *Ibid.*, 1922, **5**, 583 ; *J.*, 1922, 814A.

[17] *Ibid.*, 1922, **5**, 235.

A comprehensive series of tests on the grading of glass ware has been carried out by W. L. Baillie and F. E. Wilson.[18] With suitable modifications the apparatus used would be of service in the ceramic industry, particularly as regards the test for resistance to acids and alkalis. These factors are becoming increasingly important for hotel ware, which has to stand the hard usage of mechanical washing appliances.

It is remarkable that the apparently illogical process of drying a clay completely, prior to damping it before feeding into the centrifugal grinder, has not received earlier attention from ceramic engineers. However, H. Spurrier[19] now puts forward a suggestion to remedy this anomalous procedure. By modifying the dryer, he finds that, as soon as the water-content has been reduced to the requisite quantity, the clay can be removed from the racks and ground; thus the intermediate damping is eliminated and considerable economy both of heat and time is effected. He also claims that the dust prepared in this way is superior to that produced by normal methods. Furthermore, an interesting and somewhat novel development is foreshadowed; the clay is to be taken direct from the presses and ground in the mill, and a blast of hot air is to be directed through the column of dust in order to reduce the water-content to working requirements. But the author makes no suggestion as to what type of mill is to be used in order to grind a clay containing, for instance, 20% of moisture to dust. His paper, however, is full of interest, for it is along lines such as those indicated therein that ceramists must look for further progress in the semi-dry process.

An attempt has recently been made to overcome a disadvantage which is common to many types of tunnel dryers, and the idea has been patented.[20] The patentees, W. J. Gardner, J. Holland, and S. Gardner, claim that any portion of the moving train may be disconnected and subjected to any special drying conditions as required. This should prove a welcome facility.

Of recent years considerable attention has been devoted to firing technique in connexion with the production of the heavier types of ceramic products, such as terra-cotta, roofing tiles, etc. A number of systems have been suggested and tried, two of which deserve particular mention, since they appear to be of a promising nature. The first is described by W. W. Itner,[21] who gives interesting data regarding the application of induced draught by means of a portable exhauster. In the second system, introduced by J. L. Carruthers,[22] specially designed hollow firebars are used in connexion with a portable forced-draught equipment. In both cases very considerable economies are claimed in regard to time, labour, and fuel costs, while the proportion of best ware produced is increased. Manufacturers in other branches of the industry will no doubt wish to test the possibilities of such apparatus, since little capital expenditure is entailed in comparison with the results attained.

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[18] *J.*, 1922, 45T.

[19] *J. Amer. Ceram. Soc.*, 1922, **5**, 151; *J.*, 1922, 295A.

[20] E.P. 175,698; *J.*, 1922, 328A.

[21] *J. Amer. Ceram. Soc.*, 1922, 5, 721

The extended ground space required by the usual type of tunnel kiln often constitutes a serious drawback to its installation on an existing factory. Many schemes have been put forward from time to time to cope with this difficulty, and in a recent patent[23] a further, and somewhat ingenious solution is suggested. The new tunnel is to be widened so as to receive the trucks at right-angles to the walls of the kiln. The roof drop arches are to be extended in order to register with the top of the trucks. This will insure longer and more complete circulation of the combustion gases.

An attempt to produce from gas generators flames resembling those obtained in coal-fired furnaces is indicated in a recent patent[24] by the Siemens-Schuckertwerke. An auxiliary furnace is employed, in which resinous materials are burned, and the product of this combustion is projected into the gaseous mixture issuing from the producer. This procedure might possibly lengthen the flames sufficiently to prevent local heating. It would also be interesting to know whether, by this method, a gas sufficiently rich in hydrocarbons might be produced to render possible the successful firing of "blue" goods with gas—a problem which still awaits satisfactory solution. H. Koppers'[25] method of utilising hot air in the cooling zone of a continuous oven system suggests interesting possibilities, for, if his claims are upheld in practice, a serious drawback to the application of the continuous system to the firing of silica bricks will have been removed. Many methods have proved to be entirely satisfactory as regards the actual firing of this product, but have failed in use owing to the losses incurred during cooling.

Attention may here be drawn to an insulating door (to be used in conjunction with the existing door) for enamel kilns. This is indicative of the enthusiasm with which pottery manufacturers are studying the question of possible fuel economies. The appliance[26] consists essentially of an asbestos mattress, by the use of which, it is claimed, greater uniformity of temperature, accompanied by a saving in fuel, is obtained.

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[22] *Ibid.*, 1922, **5**, 449.

[23] E.P. 177,651 ; *J.*, 1922, 417A.

[24] G.P. 353,857.

[25] G.P. 347,672 and 347,675.

[26] *Pot. Gaz.*, 1922, **47**, 1669.

The burning of blue engineering bricks in intermittent ovens is, as is well known, an extremely wasteful operation. However, at least one continuous chamber kiln, if report[27] be true, is firing this type of product satisfactorily. The quality of the ware is said to equal that produced in the older type of kiln, while the fuel consumption is, of course, considerably reduced.

For relatively low temperatures, continuous annular muffle kilns have given every satisfaction in the ceramic industries, their chief drawback being the temperature limit to which their successful operation has hitherto been confined. A highly significant development is, however, foreshadowed in a paper by Sir A. Duckham.[28] It is claimed for the patented kiln that temperatures in the region of 1100°–1200° C. can readily be maintained; this, of course, indicates that a problem which has absorbed the attention of kiln designers for a long time has actually been solved. At present enamelled fireclay ware, glazed bricks, etc. are, with few exceptions, fired in intermittent ovens, so that the new kiln opens up wide possibilities.

An interesting development of the chamber type of continuous oven is outlined in a recent patent by Woodhall, Duckham, and Jones, Ltd., and A. M. Duckham.[29] The usual type of bag is replaced by a central burner, which is not " tied " into the structure, so that repairs can be quickly carried out. It is claimed that the gases divide and spread laterally and downward, thus ensuring uniform heating.

A novel process of burning pulverised fuel, in which Portland cement is obtained as a by-product, has been patented in Japan by T. Fujiyama.[30] Lime and small quantities of quartz, or other similar substances, are mixed with pulverised fuel in such proportions that they form Portland cement with the ashes. The mixture may be burned with air-blast to heat boilers or other apparatus and at the same time to produce cement clinker. On the face of it, the method appears to be ingenious, and, if it should prove capable of application industrially, will undoubtedly lead to great economies.

The method of economising in fuel by securing effective control of draught conditions in a kiln or furnace has received much attention of late. A. Monnier[31] has now patented an automatic draught regulator which has been in successful operation for two years on a French works. It is an ingenious apparatus, and its behaviour under actual working conditions will be watched with interest by ceramic engineers.

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[27] *Brit. Clayworker*, 1922, **31**, 21.

[28] *Engineering*, 1922, **114**, 534 ; E.P. 176,834-5.

[29] E.P. 176,419 ; *J.*, 1922, 328A.

[30] J.P. 43,420, 1922.

[31] E.P. 185,667 ; *Rev. Mat. Constr. Trav. Pub.*, 1922, No. 154, 104B.

During the past year the problem of smoke abatement has loomed largely in public discussions appearing in the daily press. It has, in fact, become a question of paramount social importance in all civilised countries. S. Momoki[32] states that he has long been investigating various methods of dealing with the difficulty in Japan. He expresses the opinion that the most promising results are obtained with tunnel kilns fired with gas under pressure from a producer.

The same author[33] discusses the relative merits of tunnel kilns and of the ordinary round ovens. The first large Dressler kiln to be installed in Japan was completed in August, 1920, and for seven months gave perfect satisfaction. The writer agrees with the opinion (now almost universally held) that, though the initial cost of installation is probably about three times as high as that for round kilns of the same capacity, this excess of fixed capital for tunnel kilns is outweighed by their general advantages.

In common with other countries, America is now devoting considerable attention to the question of firing technique, and in an interim report recently published[34] it is made abundantly clear that rapid strides are being made with various continuous firing systems. No fewer than 60 kilns have been noted as actually in use, and there are others under construction. It will be interesting at a later stage to compare the data collected by the various institutions; furthermore, the information should be of great value to those manufacturers who intend to adopt some form of continuous firing.

The important subject of glazing has received the attention of various workers. The production of ware which shows no tendency to craze is the aim of whiteware manufacturers, and various tests are in general use, the object of which is to obtain a relative indication of the liability of ware to craze when in use. These tests are nearly always designed to impart a sudden shock to the test piece. However, it is refreshing to find that F. H. Riddle and J. S. Laird[35] attack the problem from an entirely different standpoint. It is well known that a crazed piece of pottery is mechanically weak, and the new method is based upon this fundamental factor. The points which appear to warrant special attention are, firstly, the marked increase in the tensile strength of the well-glazed specimens compared with the unglazed pieces, and secondly, the remarkable decrease in strength as the crazing increases. The authors state that the decrease in strength is not due to diminished interaction between the body and glaze, but rather to increased strain due to the modification of the coefficient of expansion. It is to be regretted that the glaze recipes were not included in the report, since their exclusion prevents any conclusions being drawn by other observers. The authors might, with advantage, extend their investigations to the subject of peeling, for it is well known that this fault, like crazing, also decreases the mechanical strength of ware.

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[32] *J. Jap. Ceram. Assoc.*, 1921, 349, 474.

[33] *Ibid.*, 1921, 347, 385.

[34] *J. Amer Ceram. Soc.*, 1922, **5**, 602.

[35] *Ibid.*, 1922, **5**, 500.

A number of eminent ceramists, who have investigated the causes of crazing and peeling, have concluded erroneously that the lack of agreement between the coefficients of expansion of the body and glaze is the sole cause of the fault. The remarks by A. Granger,[36] however, are a timely reminder that the " buffer " layer formed by interaction between body and glaze, the elasticity and the " viscosity range " of the glaze employed, also have an important bearing on this troublesome subject.

The difficulties with which the ceramist has to cope are numerous and varied, and many are the solutions gratuitously offered. But it is rare that we find such positive and dogmatic statements as in the literature dealing with the causes and cure of " fish-scaling " of enamels. J. S. Grainer[37] considers that (*a*) the type of clay used as a flotative, and (*b*) the firing conditions are the primary factors upon which the appearance of this fault depends. He is of opinion that the physical properties of a clay, particularly its capacity for remaining in suspension, are of greater moment than its chemical composition. This being so, it is not clear why experiments were not tried with osmosed or colloidal clay. It is, of course, unfortunate that fish-scaling in enamelled ware, like crazing in pottery, may be retarded sufficiently long for the goods to reach the customer before the defect becomes apparent. B. T. Sweely[38] also has a further informative contribution to this question. In his experiments he removed the enamel from one side of an apparently sound piece and found that fish-scaling developed on the remaining undisturbed surface. He therefore concludes that the trouble arises owing to varying coefficients of expansion between stock and enamel, a result which recalls the work of Danielson and Soudar, referred to in these Reports last year. In a discussion of the author's results, it was pointed out that volatilisation of certain of the ingredients might account for some of the discrepancies in the reported results. But it may also be noted that the addition of materials which, from the point of view of expansion, would be expected to aggravate the defect, might at the same time increase the elasticity and thus indirectly enhance the strain-resisting capacity of the enamel.

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[36] *Céramique*, 1922, **25**, 329.

[37] *J. Amer. Ceram. Soc.*, 1922, **5**, 94.

[38] *Ibid.*, 1922, **5**, 618.

The effect of variations in the composition of ground-coat enamel on its adherence to iron is discussed by a Japanese worker, S. Mori.[39] The adhesive capacity was measured by means of the impact test, an enamel which had proved very good in practice being taken as a basis of the experiments. Some useful and interesting results appear to have been obtained, and it is concluded that the resistance to chipping is reduced by increasing the silica or boric acid content, and increased by the addition of alumina. Further, the adherence of the ground coat is strengthened by an increase of soda, potash, or lime up to a certain point, beyond which the effect is reversed.

The modern tendency toward the production of " freak " glaze effects on art ware is reflected in a contribution by R. F. Watkin.[40] He has studied the composition of glazes in relation to their susceptibility to vaporous lustring, his results indicating that, in general, glazes high in lead and low in lime are the most satisfactory for this purpose. It is unfortunate, however, that the author did not make use of quantitative methods in applying the reducing agents, for in all probability the results would vary considerably according to the volume of reducing vapours admitted to the kiln. Furthermore, a study of the effect of convection currents during the reducing stage would have enhanced the value of the work greatly.

A short reference may here be made to the so-called cold-glazed " Kerament " tiles. In view of the somewhat startling claims put forward by the manufacturers and vendors, it became imperative that thorough and systematic comparative tests should be undertaken. Two independent series of investigations were made by C. Tostmann[41] and by the Materialprüfungsamt, Berlin, and the results, though differing widely in certain respects, show very clearly that, with the exception of a few minor advantages, the cement tiles are in no way comparable with glazed earthenware as regards durability, resistance to acids, etc.

Interesting information is provided by N. Heaton[42] on the use of titanium as a pigment in paints. His results indicate that a mixture of 25% of titanium dioxide and 75% of barium sulphate gives excellent results in practice, possesses high chemical stability, is non-toxic, and is unaffected by hydrogen sulphide.

A useful contribution to our knowledge of "liquid" gold comes from the pen of P. P. Budnikov.[43] The available data bearing upon this subject are undoubtedly somewhat misleading; in many cases a mere repetition of recipes is all that is given, without sufficient indication of the method of preparation, which, after all, is the most important factor in the process.

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[39] *J. Jap. Ceram. Assoc.*, 1921, [343], 233 ; [344], 272.

[40] *J. Amer. Ceram. Soc.*, 1922, **5**, 28 ; *J.*, 1922, 217A.

[41] *Keram. Rund.*, 1922, **30**, 213 ; *J.*, 1922, 592A.

[42] *J.*, 1922, 216R.

[43] *Ber. Polytech. Ivanovo-Wosniessensk*, 1922, **6**, 211 ; *J.*, 1922, 755A.

R. Rieke and W. Paetsch[44] have compounded a series of colours on the RO,R_2O_3 basis. After calcining the mixture at specific temperatures, the free, or unaltered oxides were removed, and it was found that the residual products conformed in every case to the true RO,R_2O_3 formula. For the most part they proved very suitable for use as underglaze colours. This work recalls the earlier investigations of Seger and other ceramists on the subject.

An alternative method of determining tensile strength is suggested by R. Rieke and M. Gary.[45] Circular test pieces constricted in the centre, *i.e.*, of approximately dumb-bell shape, are tested in a machine, the jaws of which are arranged transversely or at right-angles to each other. Details of an impact testing machine suitable for porcelain are also supplied in the concluding portions of the report. The first test apparently overcomes one of the defects common to the usual methods of measuring tensile strength, viz., the difficulty of making test pieces—a factor of considerable importance. The actual data supplied by the authors would have proved of much greater value, however, if information regarding the composition of the bodies tested had not been withheld.

It has long been recognised in ceramics that the physical properties of the raw materials and of the finished product are at least equal in importance to the chemical composition. The results of work carried out by W. Steger[46] confirm the accuracy of this accepted axiom in a marked degree. His investigations were undertaken with a view to determine the effect of replacing Norwegian quartz by various other forms of silica available in Germany, including crystal sand and geyserite. In no case was the translucency of the final product comparable with that obtained with the Scandinavian material.

An improved method for the production of fused silica or alumina filaments is outlined in a patent by M. de Roiboul.[47] Filaments of 0·005 mm. diameter are extremely flexible, and it is claimed that the electrical properties are far in advance of those of other materials used for similar purposes.

BUILDING MATERIALS.

A. B. Pite[48] again directs attention to the use of ceramics as a facing for ferro-concrete structures. Fayence combines durability and cleanliness in a manner not nearly approached by any other building material. It is a mistake, in the author's opinion, to copy granite forms in ceramics. In order to popularise the medium, it is proposed that a school for the study of architectural ceramics should be formed. With regard to the question of relative costs, it should be borne in mind that the high prices of terra-cotta ware are mainly due to the abnormal shapes and sizes of the pieces employed and to the lack of uniformity generally. Manufacturers would welcome the decision to utilise smaller blocks, preferably in units not larger than standard bricks.

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[44] *Ber. deuts. keram Ges.*, 1922, **3**, 147 ; *J.*, 1922, 592A.

[45] *Ibid.*, **3**, 5 ; *J.*, 1922, 591A.

[46] *Ibid.*, 1922, **3**, 50.

[47] E.P. 165,052 ; *J.*, 1922, 142A.

[48] *Trans. Ceram. Soc.*, 1922, **21**, 328.

Considerable attention has been paid during recent years to the question of the preservation of stone used for architectural purposes. In discussing the fundamental causes of the disintegration of rock surfaces, N. Heaton[49] states that sulphur dioxide is the potent factor. His conclusions are that, in general, limewashing is a satisfactory preservative, except for stones of a close uniform texture, for which he recommends fluosilicate.

The causes of cracking and disintegration of Portland cement concrete are ably discussed by R. E. Stradling,[50] who points out that the reasons involved are numerous, and not well defined. He concludes that by far the greater number of failures are due to faulty workmanship rather than to bad materials.

R. Feret[51] reports the conclusion he has arrived at after carrying out a long series of experiments designed to test fully the effect of the inerts present in hydraulic mortars. He states that in the crushed rock type of filler it is the physical properties which are of moment and not the chemical composition.

Reference is made to an alumina cement by H. S. Spackman.[52] This material is manufactured in France and is slow setting. Unlike Portland cement, however, it hardens quickly. Its properties make it very suitable for many engineering purposes, particularly as it is said to be unaffected by sea water.

That the possibilities of concrete have not yet reached finality is indicated in a report by E. Haimovici,[53] who gives a descriptive account of the methods of manufacturing hollow concrete poles for supporting electric cables etc. Mention is made of poles 60 ft. in length, from which it must be assumed that the working details have attained an advanced stage.

Details are given by P. Atterfelt[54] of a new wooden fibrous material, which, he states, can be sawn and planed as readily as ordinary timber. In addition it has twice the insulating capacity of wood. If, as is intimated, its cost is only one-quarter that of brick, there is a distinct possibility that it may prove a serious competitor to ceramic wares of certain kinds.

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[49] *Quarry*. 1922, **27**, 56.

[50] *Concrete and Constr. Eng.*, 1922, **17**, 393, 475.

[51] *Rev. Mat. Constr. Trav. Pub.*, 1922, Nos. 150-2, 45 *et seq.*

[52] *Rock Products*, 1922, **25**, Nos. 16, 30; *Cement Eng. News*, 1922, **34** Nos. 10, 18.

[53] *Tonind.-Zeit.*, 1922, **46**, 1113.

[54] *Raw Mat. Rev.*, 1922, **1**, 54.

The possibilities of sand-lime bricks have not been thoroughly exploited owing to the lack of fundamental data relating to the materials used. W. Drakebusch[55] has undertaken an investigation in which varying types of lime were used in conjunction with a standard sand. In general, he concludes that hydraulic limes are preferable to white lime. His experiments with aged bricks suggest that the compressive strength is greatly increased by ageing.

In general practice, the ultimate strength of cement is tested after a somewhat lengthy period. Occasionally this procedure has serious drawbacks, as, for instance, when a definite time schedule has to be adhered to. R. B. Young and T. V. McCarthy[56] have developed a method in which the mixture is allowed to age for 28 days, at the expiration of which period the mass should exhibit a certain minimum tensile strength. The limits fixed are such that, if the prescribed standard is reached, it is considered safe to proceed with the building operations.

REFRACTORIES.

Though the demand for chrome refractories for steel furnaces is probably diminishing, research on the subject still continues. This may, perhaps, appear to be a somewhat unusual policy, but it is doubtless sound; for the more complete our knowledge of any product, the greater the possibilities of extending its application to other fields. In a discussion of the suitability of the various chrome ores for making refractories, R. E. Griffith[57] points out that a high percentage of chromic oxide is not so desirable as a low iron content and well-balanced proportions of silica, magnesia, and alumina. Chrome bricks, he maintains, show great strength under load at high temperatures, and are more resistant to slag penetration than magnesite bricks.

In general works practice it is not unusual to find that refractories are exposed for long periods to the vagaries of the weather before being put into service. Though this procedure was known to be unwise, the magnitude of the losses incurred thereby was not realised fully until the results of some eminently practical investigations, carried out by R. M. Howe, S. M. Phelps, and R. F. Ferguson[58] were made known. These workers determined the relative deterioration of various types of refractories after exposure in an open space for twelve months. They found that there was, in every case, a marked decrease in mechanical strength. W. J. Rees[59] also announces that he has conducted research work on this subject, but gives no figures.

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[55] *Tonind.-Zeit.*, 1921, **45**, 1170.

[56] *Canadian Engineer*, 1922, **9**, 263

[57] *Brick and Clay Rec.*, 1922, **61**, 180.

[58] *J. Amer. Ceram. Soc.*, 1922, **5**, 107; *J.*, 1922, 253A.

An interesting and valuable contribution has been added to the literature on refractories by C. E. Ayars,[60] who discusses at some length the factors demanding consideration in designing moulds for making refractories. The figures accompanying the paper will undoubtedly be of great service to those who have to construct moulds for the specific purposes mentioned. Incidentally, the author emphasises the importance of studying the question of the position in the kilns during firing, since the contraction in the lower parts of a setting must necessarily be modified by the superimposed weight of the upper courses. However, the statement that the weight of silica refractories does not affect the expansion during firing may be questioned, for, if the movements are restricted in a lateral direction, this factor will vary accordingly.

It is suggested by D. H. Moulton[61] that special tests are necessary to differentiate between suitable and unsuitable ladle bricks. He considers that the standard refractory tests would exclude certain bricks which are giving excellent results in practice. The reviewer has met with similar instances in connexion with other branches of the refractory industry, and it is to be hoped that the tendency toward the application of specially designed tests for each specific purpose will gradually be extended to cover all sections of the industry.

A recent patent by H. Koppers[62] introduces an unusual bonding material for silica bricks. A volcanic deposit is added in a finely ground condition to the crushed silicious materials, and it is claimed that a highly refractory framework is thus formed, producing bricks of great durability.

There is an urgent need for reliable data relating to the physical structure of tank blocks for glass-melting furnaces. G. A. Loomis[63] partially meets the demand by his study of the structure of blocks taken from stock, but unfortunately the sketches accompanying the paper show marked differences, and it is not stated what methods were adopted in the making process. In consequence, no definite and useful conclusions can be drawn from the data supplied. It may be noted here that W. J. Rees,[64] in his review of the provisional specifications, also points out the advisability of paying closer attention to the texture.

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[59] *J. Soc. Glass Tech.,* 1922, **6**, 184.
[60] *J. Amer. Ceram. Soc.*, 1922, **5**, 67.
[61] *Ibid.*, 1922, **5**, 833.
[62] G.P. 345,949.
[63] *J. Amer. Ceram. Soc.*, 1922, **5**, 102.
[64] *J. Soc. Glass Tech.* 1922, **6**, 184.

An anonymous writer to a German periodical[65] reviews the subject of refractory linings for lime kilns. He suggests that fine-grained, highly refractory fireclay bricks give the most satisfactory results, and, in common with other writers, stresses the importance of fine joints between the refractories. From his observations it would appear that the conditions as laid down by the writer would best be met by semi-dry, machine-made bricks—a type of brick which might also prove satisfactory for the lining of rotary cement clinker furnaces. It is definitely stated that silica bricks are not satisfactory, which is interesting in view of the observations made by W. F. Rochow,[66] who maintains that no reaction takes place between the lime and the silica at the temperature required for calcining limestone, and that, with proper precautions, silica bricks give a much longer life than fireclay refractories.

In a paper dealing with the testing of silica bricks, K. Endell[67] advocates the measurement of the proportion of quartz, tridymite, and cristobalite by the superposition of squared paper on the photomicrographs of the specimen, and claims a maximum error of 2%. This method, it may be pointed out, has already been tested in the case of igneous rocks, and is by no means so satisfactory as the modification of Rosiwal's method, already applied to silica bricks (*cf.* A. Scott, *Trans. Ceram. Soc.*, 1918, **17**, 188).

The breakdown of refractories under stress has received considerable attention during the past few years. In a recent contribution E. Sieurin and F. Carlssons[68] give details of the hot crushing strength of specimens containing various proportions of iron oxide, magnesia, etc. added to normal mixtures Perhaps the outstanding result is that relating to the effect of the addition of 0·08% of magnesia, which lowered the softening point by 40° C.

Further data relating to the mechanical properties of refractory materials at high temperatures are communicated by E. L. Dupuy in a paper presented at the International Science Congress at Liège. In general, his results, which are reviewed by P. Frion,[69] agree with recorded observations. However, he noted that samples crushed at 1000° C. regained, on cooling, a certain degree of rigidity.

Carborundum brick is the subject of a lengthy and interesting paper by M. F. Peters,[70] whose data on the grading of the inert and bonding materials are of great value. In common with other workers, he found it difficult to obtain quantitative results for slag penetration, but, in a general way, it may be taken that carborundum refractories are highly resistant to the action of silicious slags but are readily attacked by slags high in lime, lead, or iron. Probably the most interesting section of the paper is that dealing with spalling. The results obtained show clearly that, up to a certain point, the rate of spalling decreases with each successive addition of carborundum to fireclay. Beyond this point, further additions produce a marked increase in spalling. The author considers spalling to be a function of the thermal conductivity, the coefficient of expansion, and the tensile strength. Less convincing, however, is the theoretical discussion, the object of which is the development of a formula for comparing directly carborundum with clay bricks.

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[65] *Deuts. Töp. Zieg. Zeit.*, 1922, **53**, 290.

[66] *Ceramist*, 1921, **1**, 181.

[67] *J. Amer. Ceram. Soc.*, 1922, **5**, 209; *J.*, 1922, 416A.

[68] *Ibid.*, 1922, **5**, 170; *J.*, 1922, 416A.

[69] *Céramique*, 1922, **25**, 308.

[70] *J. Amer. Ceram. Soc.*, 1922, **5**, 181.

The later research on the more complex types of silicon refractories is reviewed by R. Flusin.[71] Of the two products which receive particular attention—" Monox " and " Fibrox "—the latter, introduced by Weintraub, should have a wide application as a heat insulator. It can be moulded readily, and when fired it has a remarkably low apparent density and is very refractory.

Y. Tadokoro,[72] in an extensive investigation of the thermal conductivity, specific heat, and thermal expansion of refractories, has reported much data. The method adopted by him for the measurement of thermal conductivity is based on the periodic heating and cooling of a test piece, such that the temperature of the heat source varies in a purely sinusoidal manner. The diffusivity, from which the thermal conductivity is readily obtained, is computed from Fourier's analysis of heat conduction. The results are, in the main, higher than those obtained by calorimetric methods (Wologdine ; Dougill, Hodsman, and Cobb ; Goerens etc.) and by certain applications of Fourier's equation of linear diffusion (Heyn, Bauer and Wetzel; Green) to the problem. Further, the "linear" increase in the conductivity of silica and fireclay material with temperature, up to 1200° C. (indicated by other investigators), is not apparent in the results of this investigation. Tadokoro notes an increase up to about 700° C, but above this temperature the coefficient of conductivity becomes approximately constant.

An unusual type of failure in refractories used in furnace-linings is reported upon by P. O. Menke.[73] The outer casing of the furnace was forced open by an abnormal expansion of the lining. On dismantling the furnace, it was noted that the face of the bricks which had been in contact with the metal was vitrified to a depth of approximately four inches. Beyond this was a central zone which had become very friable and soft. In order to elucidate the problem, chemical analyses of the different sections were made, and these indicated that 50% of zinc in the form both of metal and of the oxide were present in the refractories. This infiltration or segregation of zinc compounds was held to be responsible for the increase in the volume of the bricks. This curious phenomenon is of great significance, for it has already been noted that breakdowns in other refractories, particularly in the roofs of steel smelting furnaces, have also been occasionally due to the segregation of various compounds in certain well-defined zones. It is to be regretted that the author did not extend his investigations to include a microscopical examination of the different zones, for this would have added greatly to the value of his work.

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[71] *Ind. Chim.*, 1922, **9**, 391.

[72] *Sci. Rep., Tohoku Imp. Univ.*, 1921, **10**, No. 5.

[73] *Blast Furnace*, 1922, **10**, 116.

As is well known, the nature of the furnace lining has, in most cases, an important bearing on the quality of the product of any particular process. This point has been studied by G. E. Foxwell[74] in relation to coke ovens. His data suggest that the decomposition of ammonia is modified by the composition and texture of the refractories with which the coke is in contact. The gases condense to form surface films more readily on bricks relatively rich in tridymite, cristobalite, and calcium silicate than on those containing a large proportion of felspathic compounds. This author's observations are of great moment, and a continuation of the work would be of much value to all interested in coke-oven practice.

G. Walker[75] directs attention to a defect occurring in the refractories used in an oil-fired tunnel kiln. It was observed that the saggars, which had been placed in the line of the oil-spray, disintegrated and broke down after four firings, the normal life being seventy burns. On modifying the setting arrangement so that the spray did not actually impinge upon the refractories, the trouble ceased. As a result of experiments carried out with a view to finding suitable materials sufficiently resistant to the action of the direct oil-spray, the author found that carborundum proved satisfactory. It is also suggested that the targets in oil-fired furnaces be made of calcined diaspore.

A. T. Green[76] prefaces an investigation of the thermal conductivity of refractories at high temperature by a critical discussion of previous work on this subject. His method, which is easy of manipulation, is based on an application of the law of linear diffusion of heat. The reported values of this constant are lower than those obtained by calorimetric methods, but agree wel with the results of Heyn, Bauer and Wetzel. This investigatio proves conclusively that the thermal conductivity and diffusivity of silica and fireclay products increase with temperature, while with magnesite material the value of these constants decreases with temperature. The temperature-conductivity and temperature-diffusivity curves indicate a straight line relationship.

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[74] *J.*, 1922, 115T.

[75] *Bull. Amer. Ceram. Soc.*, 1922, **1**, 230.

R. D. Pike,[77] in a paper entitled "The need for more refractory insulators," suggests a device for obtaining a comparative measure of the thermal conductivity of refractories. The method is similar in most respects to the standard calorimetric method, the flow calorimeter being replaced by a standard thermal resistor, which purports to measure the heat flow.

Technical education in relation to the refractories industry is taken as his subject by G. W. Hefford.[78] The paper gives a clear and comprehensive statement of the meaning and purpose of technical education, and one cannot but sympathise with the author's object in striving to awaken thought and stimulate interest in a vital subject. It cannot be denied that the future development of the whole ceramic industry is dependent in the highest degree upon thorough and scientific investigation.

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[77] *J. Amer. Ceram. Soc.*, 1922, **5**, 555.

[78] *Brit. Clayworker*, 1922, **31**, 230.

IRON AND STEEL.

By C. O. BANNISTER, Assoc.R.S.M., F.I.C.,

Professor of Metallurgy, University of Liverpool.

THE depression in the iron and steel industry noted in the last report has continued more or less during the whole of 1922, but happily, towards the end of the year signs are not wanting that a slow improvement is taking place. This is evident from the following tables, which are a continuation of those given in last year's report. The figures have been taken from the Bulletins of the National Federation of Iron and Steel Manufacturers :—

Production of Pig Iron in the United Kingdom.

(In thousands of tons.)

Month and year.	Hæmatite.	Basic.	Foundry.	Forge.	Total including alloys and other qualities.
1921—					
Sept.	47·4	48·1	49·1	10·7	158·3
Oct.	80·2	63·3	74·5	13·6	235·5
Nov.	90·3	80·5	79·1	15·0	271·8
Dec.	92·4	81·5	78·6	13·8	275·0
1922—					
Jan.	102·9	84·7	68·3	16·9	288·0
Feb.	101·8	90·1	69·0	20·0	300·1
March	149·3	113·0	86·0	20·1	389·8
April	152·9	124·7	80·8	16·7	394·3
May	137·7	146·7	78·8	20·3	407·9
June	109·7	139·2	78·9	18·4	369·2
July	111·4	147·1	91·0	21·0	399·1
Aug.	120·2	137·4	102·2	29·9	411·7
Sept.	123·7	137·8	113·4	25·9	430·3

Production of Steel in the United Kingdom.

(In thousands of tons.)

Month and year.	Open-hearth. Acid.	Open-hearth. Basic.	Bessemer. Acid.	Bessemer. Basic.	All other ingots and castings.	Total.
1921—						
Oct.	130·2	256·1	12·4	2·6	4·1	405·4
Nov.	133·8	257·1	30·8	17·1	5·0	443·8
Dec.	120·1	222·7	23·6	10·4	4·2	381·0
1922—						
Jan.	96·2	190·9	27·2	8·8	4·4	327·5
Feb.	124·9	241·4	31·4	16·3	4·8	418·8
March	162·9	310·3	46·5	24·7	5·0	549·4
April	118·6	232·0	33·0	17·3	3·3	404·2
May	124·0	286·6	25·9	22·3	3·5	462·3
June	106·9	257·6	10·3	21·5	3·9	400·2
July	128·4	294·9	19·1	24·7	6·0	473·1
Aug.	159·9	315·4	27·7	19·5	5·9	528·4
Sept.	157·3	350·4	23·9	17·2	7·1	555·9

MANUFACTURE OF IRON.

In view of the appalling industrial conditions, the realisation of the necessity for reducing the cost of production by more economical working, and the fear of severe competition from various quarters for the world's markets, it is not surprising to find that much attention is being given to problems connected with the production of iron and steel on a large scale. The details of actual practice vary enormously, even in the same district, and it is difficult to form a definite opinion as to the merits of different methods of procedure, even when full details are available.

In his presidential address before the Iron and Steel Institute, F. Samuelson[1] draws attention to many of the problems of blast-furnace work and discusses many points which must be of vital interest to our blast-furnace managers at the present time. Probably the most important matter dealt with in this address is the question as to what extent the known deficiencies of British plants suggest a policy of scrapping and rebuilding, and on the other hand to what extent an improvement may be made with a moderate expenditure of capital. It is suggested that large expenditure should not be made unless a gross return of 20% on this expenditure is certain. The present capacity of all the blast furnaces in the United Kingdom is about 12 million tons per annum, and the maximum actual production has been ten and a quarter million tons, showing that we have an existing reserve of nearly 20%. Of the 278 furnaces workable at one time in England and Wales, 115 produce under 750 tons per week, with an average of 500 tons, and 163 produce over that amount, averaging 1000 tons per week. The difficulties met with in attempting to modify the old plants with a view to obtaining greater output are clearly indicated, for if the engine power is increased the stove power is insufficient, and if this difficulty is overcome the mains and connexions are not large enough for the increased volume of air. If by partial scrapping all these difficulties are overcome, the yard is frequently found too small for the increased traffic. In most cases there appears to be no action possible between leaving moderately well alone, and complete scrapping.

The question as to the largest desirable output of furnaces is dealt with, and some details are given of furnaces producing 500 and 600 tons of pig iron per day. With regard to the great changes which have been made in the "lines" of the furnaces, J. E. Johnson[2] is quoted to sum up the position thus: "The boshes have been lowered virtually 50%, the hearth has been increased about 50%, and the angle of the bosh has varied from 70° to 80°. The top diameters have been changed but little, as have the heights, practically all the later ones being 90 ft. These changes have taken place with an increasing rate of production, the net result of which has been to increase the tonnage per furnace to three times that of a generation ago."

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[1] *J. Iron and Steel Inst.*, 1922, **105**, 29.

[2] "Principles, Operation and Products of the Blast Furnace," p. 134.

The question of modern blast-furnace practice is also dealt with by A. K. Reese,[3] who outlines the basis upon which modern blast-furnace practice has been built up and shows the improvements in results, both as respects output and economy, which would result by their adoption in localities where the older practice is still in vogue. The object sought by the application of modern methods is summed up as follows: Consistent with quality, to produce the greatest possible economical quantity; and as any material increase in quantity has a direct and favourable bearing upon economy, this description of the object of modern blast-furnace practice may be condensed to—the attainment of the greatest possible quantity consistent with quality. The author lays special stress on the necessity for the suitable preparation of the materials to be charged, a matter which has been somewhat neglected in the past in British practice. The essential conditions of satisfactory operation of blast-furnaces are that there shall be as nearly as possible uniformity of chemical reactions and of physical movement of materials in the furnace. It is, of course, impracticable to obtain for blast-furnace use, materials of perfectly uniform size and density, but it is possible to approximate to this by suitable preparation. It is suggested that the coke used should not exceed 4 to 6 inches in size, and be free from dust, the iron ore should be 3 to 4 inches and the limestone 4 to 6 inches. The contentious question of the value of dry blast is dealt with, and it is pointed out that several of the plants originally installed have been used only intermittently, in the summer months, or have been discontinued entirely. The improvement of results by the use of dry blast is universally agreed upon, but there are differences of opinion as to the degree of economy obtained. It is suggested that there is a close relationship between dryness of the air and the maximum temperature of blast it is possible to use. With natural moist air the maximum temperature of the blast which can be used with satisfactory and smooth running of the furnace is about 560° C., and any increase in this temperature results in "stickiness," "hanging," and irregular movement of the materials in the furnace. With dry blast, on the other hand, it is possible to use blast at 850° C. with smooth running and considerable economy. The design of blast-furnaces receives attention, and the principle changes are summarised as follows:—a shaft batter of 1 in 13·5 instead of 1 in 24, a low bosh (12 ft. above top of crucible instead of 24 ft.), large hearth diameter (18 ft. instead of 10 ft.), and steep bosh angle (80° instead of 70°).

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[3] *J. Iron and Steel Inst.*, 1922, 106, 9.

An important paper dealing with the influence of the physical condition of the blast on the working of blast-furnaces is published by M. Derclaye.[4] The economy derived from the use of hot blast is incontestable, but the additional economy obtained by heating it from 400° to 900° C.—45 kg. per ton of pig—is much smaller than that derived from heating it from 300° to 400°, which was found to be 84 kg. per ton of pig. It is concluded that there is not sufficient benefit derived from heating the blast beyond 800° to warrant the increased cost involved.

The question of dry blast is also considered by this author, and the conclusion is arrived at that in some circumstances the drying of the blast cannot be made to pay. It is suggested that the economy shown in the original Gayley experiments was largely due to the fact that a higher blast temperature was used, and it is stated that moist air heated to 700°, and dry air heated to 363°, have identical influences on fuel economy. The results of experiments on the effect of enriching the air used with oxygen are given, and on a 100-ton furnace; with oxygen enrichment in the ratio of 21 : 23 the fuel economy realised was 2·5–3%, and the yield increased 12%. Calculations show that the advantages to be obtained by enriching the blast grow less in proportion as the oxygen percentage is increased.

One of the most important of the details of blast-furnace practice is the filling and proper distribution of the charge. D. E. Roberts[5] deals with the two lines on which the mechanical charging of blast-furnaces has developed, viz., by means of the skip and the bucket. He gives details of a few of the best known examples of each and a general comparison of the two. The distribution of charge due to properly controlled hand-filling is ideal, and the early attempts at replacement were on skip lines. It was soon found that, owing to the separating effect of the skip, serious errors in distribution took place. Methods were introduced to remedy these defects in the form of revolving tops, some of which are giving fairly satisfactory results. The author favours bucket charging, which is mechanically quite as serviceable as the skip and affords the great advantage of a free, simple, and open furnace top, no mechanism being needed to rearrange the charge and prevent bad distribution.

Direct Process.—Processes designed for the direct production of iron receive attention from time to time and much has been heard unofficially of the Basset process.[6] The novelty of the process is the claim that the furnace being fired by coal dust, the carbon is burnt to carbon monoxide, and not to carbon dioxide, and that the hydrogen is not burnt so that re-oxidation of the reduced iron is avoided. F. Wüst[7] criticises the claims and shows that the above-mentioned conditions would require a high temperature and excess of carbon such as is used in gas producers, the gases from which, however, are not free from carbon dioxide, although the firing conditions are more favourable, therefore the Basset claim is not practicable. Calculations made by the author show that the assumptions of Basset with regard to the process of combustion cannot be attained in the continuous melting of iron and that it is not possible to prevent re-oxidation of the metal. If the ore contains a considerable amount of gangue, the reduction of the iron is made difficult, and a part of the reduced iron will contain slag. A material balance sheet shows that under the most favourable conditions the coal consumption must be greater than the 500 kg. per ton claimed. A heat balance sheet shows that the Basset process is not so economical as the blast-furnace, and in addition the energy available from the waste gases is only 11·4 h.p.-hrs., as compared with 15·6 h.p.-hrs. for the blast-furnace, per ton of metal produced in 24 hrs.

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[4] *Rev. Univ. Mines*, 1922, **15**, vi., 1; *J. Iron and Steel Inst.*, 1922, **106**, 300.

[5] *J. Iron and Steel Inst.*, 1922, **105**, 51.

[6] U.S.P. 1,360,711; E.P. 132,622; *J.*, 1921, **48A**, 589A.

MANUFACTURE OF STEEL.

The results of an important investigation of open-hearth steel practice have been published by F. Clements,[8] who has conducted his experiments in a 60-ton Siemens furnace. The interest taken in this paper and the amount of discussion devoted to it are indications of the anxiety existing for the introduction of methods of working which are most efficient and economical. It is pointed out that the need for systematic research work into all the operations connected with the production of steel in the open-hearth furnace becomes evident when such an investigation is undertaken, owing to the paucity of reliable and consistent data, and a combined effort ought to be made by steel makers to systematise similar investigations. A complete examination is made of the chemical balance of the operations. One of the striking features in this connexion is the large amount of oxidation of carbon, silicon, phosphorus, and manganese which takes place during the melting period. The heat balance, deduced from the chemical balance, is considered, and the advantage of charging molten metal is clearly shown, for the heat brought in by the molten metal is 40·5% of the total shown and much less than the quantity which would have been required to melt it. The overall thermal efficiency of the process amounts to only 16·98%, indicating serious heat losses which are allocated as follows: Radiation from bath and port ends 44·2%; radiation from regenerators, 15·5%; radiation from flues, 4·1%; heat loss with gas to chimney, 36·2%. The heavy radiation loss which takes place from the furnace body is entirely dependent on the temperature ruling in the bath, the area of the radiating surfaces, and the conductivity of the material used in the construction of the furnace. It is pointed out that after melting, the heat contributed by the exothermic reactions involved in the removal of the elements is considerable, and by an increase in the temperature ruling in the bath several advantages are secured, for example, the slag is maintained in a more fluid and workable condition, the time of working is reduced, and greater advantage is taken of the heat of chemical reaction. A higher working temperature in the furnace may be attained by reducing the quantity of excess air admitted or by regenerating the air and gas to a higher final temperature. The efficiency of the system of regeneration is critically examined and the various factors involved in an efficient system are indicated. The fuel consumption used in the calculations was 3 cwt. per ton of steel, but, if radiant heat losses were prevented, it is possible that the consumption would not be greater than 2 cwt. per ton of metal. A design for a 100-ton furnace is suggested, in which the usual positions of gas and air uptakes are reversed and the gas reverse values are as near the regenerators as possible, and arranged to shut off the supply to the furnace whilst reversal takes place.

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[7] *Stahl u. Eisen*, 1921, **41**, 1841; *J.*, 1922, 59A.

[8] *J. Iron and Steel Inst.*, 1922, **105**, 429; *J.*, 1922, 550A.

A valuable critical comparison of the manufacture of steel in three types of furnaces—*viz.*, the Talbot, Wellman, and Martin, is made by J. Puppe.[9] The results were obtained at Witkowitz, where coke-oven gas is mixed with producer-gas for use in the steel furnaces. As the hearth of the Talbot furnace remains covered with charge, the durability is greater than that of the Wellman or Martin furnaces, and the consumption of refractories is less. The method of working the three furnaces and the progress of melting as regards metal and slag are shown in a series of diagrams. The dephosphorisation of the mixer iron in the Talbot furnace takes place in 1¾ hours as compared with 3¾ hours for the Wellman and Martin furnaces. The durability of the ladles in the Talbot process is also greater, as no slag goes into them. All three furnaces seem equally good as regards quality of material in the range of steels made. The most suitable proportion of scrap was found to be, Martin furnace 30–40%, Wellman furnace 20–25%, Talbot furnace 5–15%. The ferromanganese consumption is least in the Talbot furnace. The consumption of oxide additions and lime is greatest in the Talbot process and least in the Martin. The fuel consumption is least in the Talbot. The ratio of the daily production in heats was 4·3 : 3·5 : 2·8 for the Talbot, Wellman, and Martin furnaces respectively, the time per ton of steel being least in the Talbot furnace.

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[9] *Stahl u. Eisen*, 1922, **42**, 1, 46; *J.*, 1922, 143A.

The possibility of economising in the consumption of manganese as a deoxidiser and recarburiser of the metal in basic converter and open-hearth practice is pointed out by K. H. Eichel.[10] It is claimed that in the Thomas process, by previously melting the manganese alloy (ferromanganese in an electric furnace and spiegeleisen in a reverberatory) and adding it to the steel in the molten condition, a saving of 25–33% is obtained as compared with the addition in the solid form. The molten-metal method allows the manganese additions to be made in the ladle, and after allowing the slag to rise, a second quantity may be added to complete the deoxidation. The most suitable temperature of the steel is between 1400° and 1500° C., as at this temperature the manganese diffuses into the bath with great rapidity, exerts a maximum deoxidising power and forms a homogeneous alloy. Part of the manganese may be replaced by silicon, but this should not exceed 10%, nor fall below 5% of the total manganese added. Carbon may be used instead of silicon. In the open-hearth method the manganese loss increases with the time taken for the removal of phosphorus. The rhodochrosite and fluorspar methods for reducing manganese consumption are described. The former is suitable only in the manufacture of hard steel, and for the fluorspar method the charge should be low in phosphorus, as with large quantities of fluorspar there is a danger of rapid corrosion of the furnace walls.

Some useful instructions on methods for obtaining the best results in the manufacture of nickel steel in acid open-hearth furnaces are given by W. P. Barba and H. M. Howe.[11] The steel should be brought to the desired composition in the ladle immediately before pouring into the mould and should be freed as far as possible from oxygen at this stage. To prevent segregation, columnar crystallisation, and piping, it should be poured at the lowest possible temperature, slowly at first, then as rapidly as possible. External cracking is prevented by tapering the mould so strongly that the ingot readily frees itself immediately after pouring, while internal cracking is avoided by removing the ingot from the mould as soon as possible, allowing to cool in ashes, and by toughening, by subjecting it to a series of light reductions under a hammer or press. To prevent retention of inclusions in the steel, which is a well-known trouble with nickel steel, the metal should be deoxidised as fully as possible by means of pig iron at as high a temperature as the furnace will permit, then further deoxidised by means of silicon before adding manganese, and finally it should be held in the ladle for a sufficient length of time to permit the inclusions to rise to the surface.

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[10] *Montan. Runds.*, 1921, 13, 441 ; *J.*, 1922, 178A.

[11] *Iron Trade Rev.*, 1922, 70, 749, 893, 1117 ; *J.*, 1922, 143A.

FOUNDRY PRACTICE.

At the annual general meeting of the British Cast Iron Research Association, held on November 24th, Lord Weir dealt with the general trade depression as regards foundry practice; he considered that the depression would not lift unless the foundries played a big part in lifting it by better processes and methods, making fewer bad castings, decreasing their cost and reducing prices to what customers could afford to pay. In no branch of engineering is it so difficult to obtain a reliable explanation and an effective permanent cure for any specific trouble than in foundries.

The difficulties of controlling the composition of iron castings are well illustrated by H. J. Young,[12] who gives tables showing the differences between analyses of irons as advertised and as received from the works. There is no doubt that the large number of important variables which have to be considered in an iron foundry, render the problem of regularity of production an extremely difficult one, but fortunately there are indications that greater interest is being taken and more systematic investigations are being carried out in connexion with foundry practice, so that an early result should be a more scientific management and control of our foundries with attendant improved results. The chief developments in grey iron foundry practice are connected with the production of semi-steel by the introduction of steel scrap into cupola mixtures.

PHYSICAL PROPERTIES OF IRON AND STEEL.

A large amount of work has been published during the past year on physical properties and allied subjects, and it becomes a difficult matter to select the material most suitable for a report of this description.

The question of variations in properties of steels at different temperatures is an important one and has received attention at the hands of several investigators. L. Guillet and J. Cournot[13] have described the results of experiments on a long range of materials at temperatures varying from -20° to -190° C., that is, the temperature of liquid air. They show that hardness increases with decrease in temperature, that brittleness at low temperatures is a characteristic of ferrite, and that pure austenite containing sufficient nickel is not brittle at low temperatures. Pearlitic steels containing nickel are very brittle at liquid air temperatures, but increased nickel additions lower this brittleness. On the other hand, H. J. French[14] has carried out tensile tests at high temperatures on some structural alloy steels and has shown that steels containing 1% of chromium withstand the weakening effect of increase of temperature to about 550° C. better than either plain carbon or nickel steel.

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[12] *Foundry Trade J.*, 1921, **24**, 497, 511.

[13] *Génie Civil*, 1922, **80**, 162.

To the methods used for the determination of hardness much attention has been given, and a notable advance in the use of the Brinell method has been made by R. L. Smith and G. E. Sandland,[15] who suggest a definition for hardness as follows :—" Hardness is proportional to the load necessary to produce a constant sized impression." It is impossible to deduce the load required to give a constant impression from the Brinell formula and the authors suggest the use of a modified Brinell number obtained as follows :—Brinell number at 1000 kg. $\times$ 0·9 + 0·4/d^2, where d is the diameter of the impression in millimetres. From this new formula also may be calculated the load required to give any size of impression. It is well known that the ball test fails with the higher hardness numbers, above 525 for example, and the authors have done good service by ascertaining that an uncut diamond with a natural pyramidal point may be used for the determination of hardness over the whole range. Each diamond used must be calibrated separately owing to the differences in shape and size.

Much material has been published on impact tests, various classes of repeated and alternating stresses, etc. A useful summary of the position of our present knowledge on brittleness and fatigue in metals has been given by C. H. Desch,[16] who suggests that it should not be long before the actual values of the resistance to tensile stress and to shear, measured between adjoining planes of the space lattice, can be computed. The author considers that when this stage has been reached, the testing of metals will have been placed on a scientific basis with the greatest advantage to the practice in mechanical testing laboratories.

The actual mechanism of hardness is a fruitful field for speculation, and in this connexion the view of Z. Jeffries and R. S. Archer,[17] that the hardness of a metal is due to the distribution of hard particles in the mass which hinder the internal slip in the metal under stress, is not considered probable by K. Honda.[18] According to Honda, hardness may be due either to molecular force or to the crystalline structure of metals. The molecular force exerted between two atoms is a differential of forces of attraction and repulsion, and a substance may be said to be hard if a variation in the relative configuration of the atoms sets up large forces between atoms. A pure metal or a solid solution being homogeneous, its hardness depends solely on molecular force. In a metal having a crystalline structure hardness increases with the fineness and strained state of structure, and for equal values in these properties, the greater the molecular force developed by a given displacement in the atomic configuration, the greater is the hardness figure. In practice cold working or overstraining results in fine crystals in a highly-stretched state while annealing relieves the strain and favours grain growth.

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[14] *U.S. Bureau of Standards Tech. Paper No.* 205E.

[15] *Inst. Mechanical Engineers J.*, 1922, No. 3, 623.

[16] *Trans. Inst. Eng. and Shipbuilders*, 1922, **65**, 21.

[17] *Chem. and Met. Eng.*, 1921, **24**, 1057 ; *J.*, 1921, 515A.

[18] *Ibid.*, 1921, **25**, 1001 ; *J.*, 1922, 18A.

METALLOGRAPHY ETC.

Attention has been called by N. T. Belaiew[19] to the great variation which exists in the distance between adjacent cementite lamellæ in slowly-cooled carbon steels. The coarseness of the pearlite thus formed is dependent on the position of a secant plane. From actual observation on a projection of lamellæ on this plane, it was found that as the angle of inclination (ω) of the secant plane became smaller, the distance between lamellæ will appear greater. It is probable that the formation of pearlite during the Ar1 transformation is due to a crystallographic rearrangement with a certain linear velocity proceeding from nuclei. New α-iron grains are built up in this way. The arrangement of cementite lamellæ in a pearlite grain is roughly parallel to the crystallographic plane of the grain. The angle of inclination (ω) may be computed from the equation $\cos\omega = \Delta_0/\Delta_\omega$ in which Δ_0 is the actual distance between lamellæ on the secant plane (o) and Δ_ω the distance on a section inclined at an angle, ω. These can be measured on photomicrographs, and it is suggested that the value Δ_0 might be taken as one of the characteristics of steel indicating the thermal conditions during the Ar1 transformation. The more uniform the heat conditions, the more constant will be the value of Δ_0.

The formation of globular pearlite during the cooling of carbon steels has received further attention, and J. H. Whiteley[20] has investigated the mechanism of its formation in relation to the changes which take place during the A1 transformation. When iron is heated, complete solution of the carbide constituent of pearlite is effected only after a period depending on the temperature above the A1 point, and the size of the pearlite grain. On cooling, any undissolved particles form nuclei in the solid solution at the transition point, and the pearlite formed is globular. The true transition point may be determined by observing the temperature at which the nuclei commence to grow. If no nuclei be present, the Ar1 transformation does not occur, even under slow cooling conditions, until the temperature has fallen below the true solubility, and it would seem that lamellar pearlite will not grow until a certain degree of supersaturation is reached. The presence of globular pearlite induces an earlier growth of lamellar pearlite in adjacent areas free from nuclei. The exclusive formation of lamellar pearlite indicates the entire absence of carbide nuclei from the solid solution. The effects on the tensile tests obtained by spheroidising the cementite are given by H. C. Ibsen,[21] the most striking result being a remarkable increase in ductility.

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[19] *J. Iron and Steel Inst.*, 1922, **105**, 201 ; *J.*, 1922, 419A.

[20] *Ibid.*, 1922, **105**, 339 ; *J.*, 1922, 419A.

The microscopical structure of steels has been examined from the standpoint of colloid chemistry by F. C. A. H. Lantsberry,[22] who suggests that the structures obtained by different rates of cooling of carbon steels may be explained as follows :—Cementite is to be regarded as the dispersed phase, and ferrite as the dispersion medium. At high temperatures the degree of dispersion is great enough to produce the molecular solution austenite. As the material cools a temperature is reached at which the dispersed phase assumes the colloidal state and troostite is formed. Troostite shows a maximum solubility in acids, and is irresolvable, even under the highest powers of the microscope. Troostite may therefore be rightly regarded as a colloidal solution in which cementite is the dispersed phase. As the temperature falls the phenomenon of coagulation occurs and sorbite is produced. Examination of sorbite under the microscope indicates that it has the structure of a suspensoid. On still further cooling, pearlite is obtained and the structure recalls very strongly the phenomenon of periodic precipitation.

The colloidal state in metals and alloys has also been dealt with by J. Alexander,[23] who suggests that the so-called amorphous phase in pure metals is an isocolloid consisting of colloidal groups of metal molecules dispersed in still more finely-divided metal. Such colloid particles are not truly amorphous, but may consist of ultramicroscopical crystals, and the expression "amorphous phase" might, with justice, be replaced by the term "colloidal phase."

As a result of recent investigations, several changes are suggested in the constitutional diagram of the iron-carbon system by K. Honda.[24] During the cooling of molten cast iron, graphite separates in the range 1130°–1050° C., that is, after the solidification of the metal. A theory is suggested that graphite is not a direct decomposition product of cementite, but is due to a catalytic action of carbon monoxide and dioxide on the cementite. The most favourable temperature for graphitisation is just below the eutectic point 1130°–1100°. The graphite line on the double diagram should therefore be omitted. The critical point A2 as determined thermally indicates only the commencement of the transformation. X-ray examination shows that iron has always the centred cube space lattice structure below the A3 point, and thus β-iron does not exist as an independent phase. The A1 line is drawn horizontally, and as in the author's view the transformation is austenite $\rightleftarrows$ martensite $\rightleftarrows$ pearlite, the martensite line is absent, as martensite does not actually come into existence except in quenched steel. The transformation of cementite (A0) is drawn as a dotted horizontal line similar to the A2 line as the transformation is progressive from the lowest temperature to 215° C.

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[21] *Forging and Heat Treating*, 1922, **8**, 300 ; *J. Iron and Steel Inst.*, 1922, **106**, 389.

[22] *J.*, 1922, 409R.

[23] *Chem. and Met. Eng.*, 1922, **26**, 54, 119, 170, 201.

[24] *J. Iron and Steel Inst.*, 1922, **105**, 381 , *J.*, 1922, 418A.

It is pointed out by K. Honda and T. Kikuta[25] that a transformation point is not a single temperature at which transformation ca occur, because, as the velocity of heating or cooling decreases th temperature of transformation varies, the tendency to the chang being small at first, increasing to a maximum and then falling awa by virtue of opposing influences, *i.e.*, the internal viscosity of th substance. The conclusion drawn from experiments on chromiu and nickel steels, in which the transformation can be retarded, i that the Ar''1 transformation is merely the retarded Ar'1 (Ar1 transformation and not a separate phenomenon.

The study of the nature of the constituents of carbon steels ha been carried further by the determination of the heats of transformation of austenite to martensite, and martensite to pearlite, b N. Yamada.[26] The heat of the transformation austenite – martensite is found to increase linearly with the carbon, and amount to 5·6 calories per gram for eutectoid steel. The specific heats o troostite, sorbite, and pearlite have the same value within the limit of experimental error, and the heat of dissolution of carbon in iro also increases linearly with the carbon content and amounts t 1130 cals. per gram of carbon.

The work of A. Westgren[27] on X-ray spectrographs of iron a different temperatures, mentioned in the last report, has been carried further, and A. Westgren and G. Phragmen[28] have shown by X-ray photograms of an iron wire heated to 800°, 1100°, and 1425° C. that within the β- and δ-ranges iron has a body-centred cubic lattice structure and within the γ-range a face-centred cubic lattice. The transformation which takes place at 900° C. (A3) is thus reversed at 1400° C. (A4). The γ-iron lattice of austenite steels is enlarged by the dissolved carbon. A steel with 1·98% C has a somewhat larger lattice when quenched from

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[25] *J. Iron and Steel Inst.*, 1922, **105**, 393 ; *J.*, 1922, 418A.
[26] *Ibid.*, **105**, 409 ; *J.*, 1922, 419A.
[27] *Ann. Repts.*, 1921, **6**, 262.
[28] *J. Iron and Steel Inst.*, 1922, **105**, 241 ; *J.*, 1922, 418A.

1100° C. than when quenched from 1000° C. The α-iron lattice in martensite also seems to be influenced by the carbon present; the range of α-iron lattice in martensite is extremely small. A steel with 0·8% C quenched in water from 760° C. is on the verge of being totally amorphous.

CORROSION.

The corrosion of iron and steel is a subject of paramount importance, and investigations are being carried out on a large scale under varying conditions with a view to elucidate problems connected with the phenomena observed, and of obtaining definite information as to the best type of material to be used under certain specified conditions. In spite of the large amount of work which has been done in the past, it is still very difficult to decide what class of iron or steel can be expected to give best service under certain conditions. The whole of this year's volume of Carnegie Scholarship Memoirs, published by the Iron and Steel Institute, is devoted to a series of reports by J. N. Friend,[29] dealing with various aspects of the corrosion of iron. The volume contains a critical survey of our present knowledge of the corrosion of cast iron, and in addition, the author deals with the protection of iron with paint against subaqueous corrosion, the influence of strain and of temperature upon the corrosion of iron, and also with the colloidal theory of corrosion.

The internal corrosion of cast iron water mains is of considerable importance, and W. Ransom[30] has shown that there are several forms in which rust appears. These have been classified as follows: (1) Coarse blotches or blisters, which increase by the addition of concentric layers, and may form deposits 1½ inches in thickness; (2) a rusty slimy mud, with a yellow tinge; (3) a graphite change in the metal, causing it to assume a spongy nature. This action may take place in spite of a protective coat, and the only safeguard is to have mains of good quality. Besides the ordinary corrosion of mains, a flocculent black slimy matter is deposited by water, containing iron in solution. If such waters are slightly acid by reason of vegetable matter, such as peat, an organism known as creaothrix develops. The germs attach themselves to the inner surface of the main and live on the carbon compounds of iron, and iron oxide is deposited during growth. The remedy for this trouble is the removal of the vegetable matter by filtration, and the iron by means of aeration.

The corrosion of iron pipes in alkaline soils has been investigated by J. W. Shipley,[31] who shows that the process is electro-chemical in nature. The process is complicated by its dependence on several variables of which the composition of the metal, the nature of the soil in contact with the metal, and the movements of the ground waters are the most important. The corrosion of cast iron by soil salts is of the graphitic softening type, and of the soil salts those of magnesium are the most corrosive. Local action induced by naturally occurring concentration cells may easily be a factor in the corrosion of iron pipes. The presence of calcium sulphate in a limey silt soil gives a slight acidity to the ground waters which promotes auto-corrosion of the cast iron due to the stimulation provided to the graphite-iron couple by the presence of the hydrogen ion.

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[29] *Carnegie Schol. Mem.*, 1922, **11**, 161 pp.; *J.*, 1922, 300R.

[30] *Foundry Trade J.*, 1921, **24**, 414.

[31] *J.*, 1922, 311T.

Sir R. A. Hadfield[32] has described the preparation and properties of the ferrous metals used in the research on corrosion by a committee of the Institution of Civil Engineers formed in 1916 to investigate the deterioration of structures exposed to sea-water. The investigation deals with 14 types of metals, which may be divided into four main sections, *viz.*: (1) rolled and forged irons; (2) carbon steels; (3) special steels; and (4) cast irons. The theories of corrosive action and the behaviour of special materials are discussed and it is pointed out that the beneficial effect of copper on the resistance of steel to corrosion is not fully established; for preventing or mitigating corrosion, the addition of copper to steel is not generally advisable. The resistance of non-rusting steel to corrosion when almost constantly wetted by sea-spray, depends on its physical constitution. Attention was called to the wastage due to corrosion, and it was suggested that of the 1860 million tons of steel produced in the period 1860–1920, 660 million tons was probably lost by rusting in use. The loss due to corrosion in 1920 was estimated at 29 million tons.

The relationship of acid attack and ordinary corrosion is of considerable importance from many points of view. The rate of solution of iron in dilute sulphuric acid is shown by J. A. N. Friend and J. H. Dennett[33] to be directly proportional to the velocity of rotation of the mixture. At 4000 revolutions per hour there is no falling off in the rate and the phenomenon is independent of the concentration of the acid. It is thus shown that the solution of iron in sulphuric acid is not analogous to the corrosion of iron in aerated water.[34] In stationary mixtures, dilute solutions of colloids, gum, etc. greatly retard the solution of the metal, while rise of temperature increases it.

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[32] *Min. Proc. Inst. Civil Eng.*, 1922, 91 pp. See also *Proc. Roy. Soc.*, 1922, **A101**, 472; *J.*, 1922, 761A.

[33] *Chem. Soc Trans.*, 1922, **121**, 41; *J.*, 1922, 179A.

[34] *Ann. Repts.*, 1921, **6**, 267.

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NON-FERROUS METALS.

By C. A. Edwards, D.Sc., and H. I. Coe, M.Sc.

Conditions in the non-ferrous industry during 1922 show a slight improvement on those which existed in 1921, and the prospects of a recovery from the depression in trade of the last two years are now more favourable. Post-war stocks of metals are diminishing and, in consequence, some of the common metals show a tendency to harden in price.

At home the metal industries have not been seriously interfered with by industrial troubles, but in America the prolonged coal strike resulted in a reduction of output; its effect was less serious than it would have been in previous years, on account of the prevailing depression. The settlement of labour difficulties on the Rand has permitted of the operating of several mines which would otherwise have been closed down, on account of the steady fall in the price of gold.

A search of the technical literature indicates that, with few exceptions, little, if any, new plant has been laid down; in fact, in most cases it has been found impossible to keep the whole of existing plant in operation. It appears that the most serious hindrances to a return to at least pre-war conditions are the instability of the foreign exchanges and the unsettled state of the international situation, and any improvement in these respects will be soon reflected in an increased demand for metals, with the consequent increase in price and production.

The Metallurgy of Copper.

New uses for copper have not developed to any marked degree, and though the future may see a largely increased demand for electrical purposes, many big electrification schemes have not, as yet, been put into operation, and present consumption shows no sign of early marked increase.

Production in America for the three first months of the year showed a steady and increasing improvement on the nine last months of 1921; at the same time production in March, 1922, amounted to less than half that of the corresponding month of 1920.

Progress in extraction has been almost entirely along the lines of hydro-metallurgical treatment. A large amount of work has been carried out during the year, chiefly in America, on the treatment of low-grade ores, and several interesting papers have been published giving the results of treatment of ore bodies on both an experimental and a large scale. An interesting review of the methods of treatment is given by H. W. Morse,[1] who discusses particularly the extraction of copper from low-grade mixed sulphide-oxide ores. He points out that while the recovery of sulphide mineral is satisfactory when using modern flotation methods, the recovery of the oxidised portion is small, and that better recoveries of oxidised copper were made before flotation methods were adopted. Where the oxidised copper is present as pure carbonate flotation after filming with sulphide often works satisfactorily, and where such a method can be applied it may be the best solution of the mixed ore problem. Unfortunately, much of the oxidised copper in the large porphyry mines is in the form of copper silicate and flotation may lead to nothing. The ore is so impregnated that a bright blue colour may mean no more than 1 or 2% of copper. Morse refers to very interesting experiments which have been carried out by agitating fine crushed ore with solvents in Pachuca tanks, precipitating the copper by means of finely-divided iron and floating the precipitated copper and sulphide together. In view of the large amount of mineral of this kind which occurs in various parts of the world, this suggestion appears most valuable.

Reference is made to the use of sulphur dioxide for leaching purposes, and it is stated that tests show the leaching results to be good, though the action on dilute silicates is much slower than that of sulphuric acid.

Ammonia, with the addition of ammonium salts, has been successfully applied at the Calumet and Hecla mine (native copper), and at the Kennecott mine (oxidised copper); in both cases the use of an acid leach is impracticable on account of the high proportion of calcite in the ore.

One of the following treatments should be successful on most classes of low-grade ore :—(1) Sulphidising flotation. Most economical if practicable. (2) In the case of certain ores with copper as sulphide and oxide in approximately equal amounts, leach out the oxide, re-grind, and recover the sulphide by flotation. (3) Leach—precipitation—flotation. (4) Heap leach as with Spanish ores. (5) Sulphatising roast for low-grade concentrates high in pyrites.

The leaching of copper ores with sulphuric acid is described by A. W. Allen,[2] who, after giving an account of experimental work conducted on an ore containing 1·4% of copper, describes a plant having a capacity of 5000 tons per day. Details of the methods of mining, crushing, and charging the vats are given. The twelve leaching vats, 88 ft. × 88 ft. × 17 ft. 4 in. deep, are constructed of reinforced concrete with wooden bottoms ; the sides are covered with 8-lb. lead protected from abrasion by 2-in. planks, and have each a capacity of 5000 tons. The ore is leached with 10% sulphuric acid, portions of the circulating liquors being withdrawn to percolate fresh charges. When almost neutral the liquors are passed to towers in which they come in contact with sulphur dioxide, which reduces iron in solution as ferric salt to the ferrous state, this reduction of ferric iron to a low percentage being essential in order to permit of successful electrolysis with the use of insoluble anodes ; ferric salts tend to dissolve the copper on the cathodes. The principal features noted in regard to the leaching operations are : (1) upward submergence and percolation ; and (2) a high rate of flow. A recovery of over 80% of the copper in the ore is anticipated. W. E. Greenawalt[3] emphasises the serious interference of even less than 1% of ferric iron in the electrolyte with the efficiency of electrolysis, and describes a method of reduction by sulphur dioxide, which he claims constitutes a marked improvement on the use of scrubbing towers. Briefly his process consists in spraying the electrolyte in a stream of hot gases containing sulphur dioxide from roasting furnaces. He suggests also the use of precipitated copper sulphide as a reducing medium.

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[1] *Min. and Met.*, 1922, **27**, 15.

[2] *Eng. and Min. J. Press*, **113**, 952.

Other papers dealing with the hydro-metallurgy of copper are those by J. Irving[4] and P. R. Middleton.[5] Irving gives an interesting outline of Spanish practice in heap leaching and makes reference to similar work which is carried out at Bisbee, Arizona, on an ore containing 0·9% of copper. He prefers for precipitation of the copper a properly constructed vat system to the launders that are employed at Rio Tinto. In another paper the same writer describes the application of sulphur dioxide to the leaching of ores of low grade, and states that recoveries up to 90% can be obtained from oxidised ores of high acid-soluble copper content and from those that require a preliminary roast ; in the latter case the solvent required is produced in the roasting operations. Middleton refers to the high solvent power of ferric salts on roasted copper ores, and the difficulties that have been encountered, owing to the precipitation of basic salts which interfere with filtering, and suggests a method of overcoming this difficulty by the removal of colloidal matter by Dorr bowl-classifiers or hydro-separators.

The application of the electric furnace to the smelting of copper ores is described by C. S. Witherell and H. E. Skouger,[6] who give an account of experiments made at Sulltjelma, in Norway. The furnace, illustrated by diagrams, is a non-tilting electric furnace suitably lined and possessing matte and slag taps, a gas vent, and carbon electrodes passing through the roof. The electrodes dip into the slag but are kept a considerable distance from the matte layer, and the heating is effected entirely by the current passing through the slag between the electrode tips. During the war smelting of dressed sulphide ore was successfully carried out in small furnaces, and a 3000-kw. furnace was built which it was estimated would smelt 100 tons of charge per day; it was not, however, put into operation on account of the poor market for copper after the war. Certain advantages possessed by the electric furnace for smelting copper ores are obvious, and the possibility of working high-silica and relatively non-corrosive slag is specially mentioned. The success of the electric furnace will clearly depend on the price of electric power as compared with that of other fuels, and there are good prospects of its use in countries possessing copper deposits and cheap supplies of power.

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[3] *Eng. and Min. J. Press*, **114**, 712.
[4] *Ibid.*, **113**, 714 ; **114**, 280
[5] *Ibid.*, **114**, 451.
[6] *Ibid.*, **113**, 356.

METALLURGY OF TIN.

The considerable increase in the price of tin, if it has not been artificially promoted, promises well for the recovery of an industry which has felt most severely the recent depression. Very little information of a technical character has been made public during the year. C. W. Gudgeon[7] gives an account of a modified treatment of a 2% tin ore by concentration at the Mount Bischoff mill in 1920–21, which has resulted in an increased extraction. Essentially the improvement consists of the recovery of a third product in the slime plant, containing 1·5–4·5% of tin; the top first foot of the pyritic portion of the reject from the various concentrating tables was found to assay slightly over 2% of tin, and this was re-treated.

METALLURGY OF NICKEL.

An illustrated account of the operation of nickel refining at the Clydach, South Wales, works of the Mond Nickel Company is given in the "Metal Industry."[8] For many years so little has been published concerning the extraction of nickel that the information given, though not entirely new, is interesting. A flow sheet of the major operations is printed.

References have been made in the daily press to experiments which are being carried out in South Wales on the production of a coating of nickel or nickel alloy on steel ingots which are subsequently rolled to nickelled plates, which it is thought may be substituted for tin plates for many purposes. Even if satisfactory results are obtained it is uncertain how far popular prejudice is likely seriously to retard nickelled plates rivalling tin plates in the industries. In the canning trades there seems to be little prospect of the latter being displaced, but there may be a useful future for the former in other directions.

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[7] *Bull. Inst. Min. and Met.*, May, 1922.

[8] *Metal. Ind.*, 1922, **20**, 149.

F. E. Lathe[9] gives methods for the determination of copper, nickel, cobalt, silica, acidity, etc., which are used in the laboratories of nickel plants. The various methods for the determination of nickel and their relative merits are fully discussed ; specially useful details of the cyanide titration method as applied to ores and products are given.

METALLURGY OF ZINC.

The year has seen a partial recovery from the collapse of the spelter industry, and a number of furnaces are now in operation in this country. There are, as yet, no indications of any revolution in the processes of smelting zinc ores. Blast roasting of ores and treatment of residues are receiving greater attention, as the low margin of profit in present-day smelting operations is forcing consideration of these matters on managements.

A. Bordeaux[10] gives an account of the Norwegian process of electro-thermic smelting in the Tharaldsen resistance furnace and the Swedish process used at the Trollhattan works.

The important progress made in recent years in the production of zinc by the electrolysis of zinc solutions continues, and Tasmania has now to be added to the list of areas in which electrolytic zinc is produced in quantity. The present potential world's production of electrolytic zinc is said to exceed 125,000 tons per annum.

It is claimed that, granted the production of a high percentage of soluble zinc in the roasting of ores, the cost of the production of zinc by electrolysis would compare favourably with the cost of smelting in retorts, as the cost of power should not much exceed the cost of the fuel required in retort smelting, while reduced labour charges and the greater purity of the product should balance the greater cost of plant. It is hardly surprising that relatively great headway is being made by electrolytic processes, more particularly in those countries where water power is available.

A paper of exceptional importance has been published by F. Laist, F. F. Frick, J. O. Elton, and R. B. Caples.[11] The authors emphasise that the zinc sulphate solutions must be quite free from metals more electro-negative than zinc, such as copper, cadmium, lead, arsenic, antimony, etc. ; arsenic and antimony are especially objectionable and their presence in the electrolyte results in a serious loss of current. The difficulty of deposition in the presence of traces of impurities is explained as being due to the greatly increased solution tendency of impure zinc in sulphuric acid as compared with that of pure zinc.

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[9] *J.*, 1922, 270T.

[10] *La Houille Blanche*, 1921, **20**, 223 ; *Rev. Mét.* (Abstracts), 1922, 207.

[11] *Proc. Amer. Inst. Min. Met. Eng.*, **64**, 699; see *Rev. Mét.*, 1922, **19**, 188, 253.

The authors follow an account of the initial laboratory experiments with a description of the plant, which was enlarged in 1918 to yield a production of 150 tons per day. The necessity for the production of a high percentage of soluble zinc during roasting and for the production of sulphuric acid to cope with the demand for solvent involved a careful study of the best roasting conditions; the temperature most favourable to a sulphatising roast was found to be a dull red heat, 550°–600° C. The soluble zinc obtained with concentrates assaying 33% Zn and 20% Fe, amounted to 85%, and with a higher grade material, for example 50% Zn and 5% Fe, it was 94%; the water-soluble zinc amounted to 14–20%.

Leaching is carried out in two stages, the first leaching being conducted with a mixture of acid from the electrolytic baths and the prepared leaching liquor. Calcines and leach liquor are agitated in a series of seven continuous Pachuca tanks; the overflow from classifiers passes to Dorr decanters to give a clear liquid, which passes to the purification tanks, and a product containing 50% of solid matter, which is subjected to a second treatment with leaching acid. In the first leach the following changes are effected: (1) three-quarters of the soluble zinc passes into solution; (2) iron is oxidised and precipitated; (3) gelatinous silica is coagulated and rendered granular by excess of base; (4) arsenic and antimony are completely precipitated; (5) 80% of the copper is precipitated as hydroxide by the excess of base (lime); and (6) most of the zinc and 20% of soluble cadmium go into solution. Purification of the liquors is based on the fact that an excess of zinc powder will completely precipitate copper and cadmium.

The electrolytic works contain six units with 144 tanks in each unit. At full charge the current density is 30 amps. per sq. ft.; the fall of potential across each bath is 3·8 volts when operating with electrolyte containing 10% of acid. The total ampèrage is 10,000, and the voltage 500, and 4½ kg. of zinc is deposited per h.-p.-day. Cathodes are stripped every 48 hrs. and give two leaves of zinc weighing 8 kg.; gelatin is added to the electrolyte so that denser deposits may be obtained.

The authors deal fully with the melting of the zinc, the production of zinc powder, and the treatment of residues.

An interesting description of a scrubber of the water-spray type for cleaning metallurgical smoke has been published.[12] This scrubber was found to yield more satisfactory results than any other type of cleaning appliance at a Ducktown smelter when applied to gases containing 6–8% by volume of sulphur dioxide, and a fume content of 2·2 lb. per 1000 cub. ft.; a fume consisting largely of zinc oxide was recovered and the cleaned gas was used for the manufacture of sulphur.

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[12] *Eng. and Min. J.*, 1922, **113**, 198.

METALLURGY OF LEAD.

The demand for lead has been comparatively keen during the year. Relatively little has been published concerning the extraction of the metal from its ores, though a certain amount of information on subsidiary processes, such as fume deposition, is to be found in the technical journals.

The development of flotation concentration processes has undoubtedly enabled production to proceed in spite of the relatively low prices which have prevailed during recent years.

METALLURGY OF GOLD AND SILVER.

No striking advances are recorded. On the Rand the decantation process in cyaniding continues steadily to be abandoned in favour of agitation and filtration processes. Production of gold in South Africa in October nearly approached the record pre-war monthly output.

W. Cullen[13] gives recent and interesting statistics concerning the output of the Rand goldfields. In 1921, 24,000,000 tons of ore was mined, producing gold of the value of £42,000,000 (including premium), or approximately 50% of the world's production. An outline of practice at one of the most successful South African plants—that of the New Modderfontein Gold Mining Co.—is given to indicate the processes which are in general use to-day. The mined ore, after spraying with water, is discharged into cylindrical trommels, which serve to separate about 40% of "fines" from the coarse ore, which is subsequently hand-picked on belts, the reject assaying less than one dwt. per ton. The coarse material, after passing through gyratory crushers, is conveyed to the stamp mill bins, from which it is fed to the battery. The pulp flowing out from the stamp battery screens passes to classifiers, which yield slimes that are by-passed to the slime department, and coarse material which is treated in standard tube mills. Selected ore pebbles are employed in the tube mills to effect crushing. The crushed product passes over amalgamated plates, which extract 45–65% of the precious metal, to cone classifiers. Sands are treated in the customary manner by percolation, and slimes in Brown agitation tanks with subsequent filtration in a Butters vacuum filter installation. Residual sands and slimes are practically barren.

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[13] *J.*, 1922, 316T.

An account is given of new methods which are to be put into operation in the extension of the Springs Mines plant, with a view of eliminating: (1) the amalgamation process; and (2) the production of sands, with a consequent large reduction in capital outlay on treatment tanks. The suggested changes consist in the sliming, in cyanide solution, of the whole of the product from the crushing plant by means of larger and improved tube mills, and then stage classification by Dorr classifiers. It is estimated that capital costs will be reduced 20–40%, and working costs 20–25%.

The chemistry of the cyanide process is given briefly, and note is made of the changes that have been brought about in the way of reduced consumption of chemicals during the last 30 years; attention is drawn to the superiority of lime over caustic soda in regard to cost and the property lime possesses of facilitating the settling of slimes. The recent operation of a refinery and mint in South Africa is also noted.

NEW ALLOYS.

At the beginning of the year the Eleventh Alloys Research Report to the Institution of Mechanical Engineers[14] was published. Like the three previous reports, it deals with alloys of aluminium and gives the most important results of extensive investigations carried out over a number of years, including the war period, when the demand for light alloys served as a great stimulus to the detailed study of aluminium alloys.

The properties of the alloy to the specification known as L5, and containing 12·5–14·5% of zinc and 2·5–3% of copper, are discussed and the characteristics of the material are made clear. When sand-cast this alloy gives a tensile strength of 12 tons per sq. in., and an elongation of about 3% on 2 in.; *i.e.*, providing the casting is thin or small. These figures cannot be obtained with large castings with thick sections. Chill castings give much better tensile properties. Weakness of this and similar alloys at high temperatures renders them unsuitable for many purposes for which light alloys are desirable, and a search was made for aluminium alloys which maintain a large proportion of their strength up to temperatures of 300°–350° C. Copper-aluminium alloys containing up to 14% of copper were found to be superior, while the further addition of 1% of manganese yielded an alloy which was actually stronger at 250° C. than at ordinary temperatures. Unfortunately, difficulties in producing these alloys in the foundry arose, so the effect of nickel was studied and ultimately an alloy containing 4% of copper, 2% of nickel, and 1·5% of magnesium was found most nearly to meet requirements. This alloy, known as "Y" alloy, was also satisfactory in other respects, and could be worked easily; in the form of rolled sheet it possessed an ultimate strength of about 28 tons per sq. in., with an elongation of over 15% on 2 in. The specific gravity was 2·79.

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[14] "On Some Alloys of Aluminium," W. Rosenhain and S. L. Archbutt; see *J.*, 1921, 851A.

The following table shows the results of a few tests on this material:—

Tensile Tests on Rolled "Y" Alloy (sp. gr. 2·80).

Material.	Condition.	Elastic limit.*	Yield point.*	Ultimate stress.*	Reduction of area. %	Elongation % on 2 in.
⅞ in. rod	Hot rolled ..	—	12·0	17·6	30·0	20·0
	Quenched from 530° C. and aged	7·7	15·4	24·1	33·0	23·0
	Cold rolled from 1¼ in., hot rolled, quenched from 530°C. and aged ..	7·7	15·2	24·2	34·0	25·0

* Tons per sq. in.

Tests on "Y" Alloy at High Temperatures.

Temp. °C.	Sand cast.		Heat-treated rod.	
	Ultimate stress.*	Elongation % on 2 in.	Ultimate stress.*	Elongation % on 2 in.
20	11	1·9	24·2	24
100	—	—	22·5	22
150	—	—	21·3	23
200	—	—	19·7	24
250	10·3	1·1	—	—
300	8·5	1·5	—	—
350	5·1	6·0	—	—

* Tons per sq. in.

It was found that the resistance to corrosion of this alloy was much superior to that of other strong aluminium alloys. The phenomenon of ageing exhibited by many alloys of this kind after heat treatment was investigated carefully, and important conclusions were deduced.

Other alloys which have recently attracted much attention are those of aluminium and silicon. Aluminium possesses a solid solubility for silicon of 0·7% and forms a eutectic, melting at 570° C., with 13·8% of silicon. L. Guillet,[15] in a discussion of these alloys,

[15] Rev. Mét., 1922, 2, 303.

states that those containing up to 12% of silicon have a specific gravity practically the same as that of aluminium; they have a silver white colour and can be easily worked. The properties of the alloys are compared with those of 8% copper-aluminium, 10% zinc, 2% copper-aluminium, duralumin, and commercial aluminium; in the cast condition the mechanical properties of the aluminium-silicon alloys compare favourably, in the worked condition they are not so good, but when subsequently annealed the comparison is again favourable. Reference is made to the remarkable results which have been obtained in America by melting the 13% silicon alloy with a mixture of alkali salts. The constitution of the alloy is completely changed and the structure consists of fine particles of silicon in a ground of aluminium. The material when cast possesses a maximum strength of more than 19 kg. per sq. mm. (12 tons per sq. in.) with an elongation of over 5%. The shrinkage is small compared with that of similar light alloys produced in the foundry, and it is suggested that the alloy would be useful for the manufacture of the cylinders of motors. In France and the United States the alloy is manufactured under the name of Alpax, and in Germany under the name of Silumin.

J. J. Curran[16] disagrees with Guillet's explanation of the modification of the structure as being due to the fluxing action on oxides, etc. of the alkali fluoride commonly used, and suggests that the modified structure is due to the introduction of sodium into the alloy by a reaction between the sodium fluoride of the flux and the silicon of the alloy. Though the evidence he presents in support of his suggestion does not appear conclusive, it receives support in a more recent paper by J. D. Edwards,[17] who gives the method adopted by the Aluminium Co. of America for modifying the structure of such alloys; it consists in the addition of very small amounts of metallic sodium, enclosed in sealed aluminium capsules, to the molten alloy a short time before casting. This writer refers to the best composition, the good casting properties, the low shrinkage, and the high resistance to corrosion of the alloys.

Edwards states that a 11% silicon "normal" alloy in the form of a hydraulic casting withstood a pressure of 200 lb. without leaking, whereas a similar casting of ordinary aluminium-copper alloy leaked at 40 lb. pressure.

Z. Jeffries[18] traces the development of these alloys and gives photomicrographs which make clear the marked differences in structure in "normal" and "modified" alloys. He discusses the physical properties and recommends a silicon content of 4–10% for the "normal" alloys and one of 8–15% for the "modified" alloys. The alloys cast well, and possess moderate strength, but do not machine so readily as standard copper-aluminium alloys. The presence of iron renders them more easily corroded, and the effect seems to be more marked in the alloys of higher silicon content.

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[16] *Chem. and Met. Eng.*, 1922, **27**, 360.

[17] *Ibid.*, 1922, **27**, 654.

[18] *Ibid.*, 1922, **26**, 370.

H. Sutton[19] draws attention to the precautions that should be taken in the analysis of these alloys, and points out the possible danger of loss of silicon during solution in hydrochloric acid, owing to the formation of volatile silicon chloride; initial solution in caustic potash is recommended.

ANNEALING AND RECRYSTALLISATION.

H. C. H. Carpenter and C. F. Elam[20] have extended their earlier work on crystal growth in pure commercial aluminium, and the results obtained are extremely interesting and significant. They have examined the influence of varying degrees of stress upon the crystal growth which occurs with subsequent annealing. As was to be anticipated from previous work, they found that there is a certain rather low critical stress beyond the yield-point which causes the most pronounced increase in the size of the crystals formed when the material is afterwards annealed. As a result of most careful observations in this direction they have been able to produce large test pieces, consisting of a single crystal in each case. This important result, which has never previously been accomplished, enabled them to determine the mechanical properties of single crystals at different orientations in respect to the tensile pull. These experiments clearly indicated the influence of orientation on the character of the slipping that took place during plastic deformation, and they have opened up a new and important field for further interesting work. One remarkable result which seems to necessitate a modification of previously held views concerning the mechanism of plastic deformation, and one which may not be without practical significance, is that a single crystal of aluminium is capable of undergoing a remarkable degree of cold work without becoming materially hardened.

Z. Jeffries and R. S. Archer[21] enumerate the laws governing grain growth in metals and put forward suggestions to explain the causes of the phenomena observed. The articles give a useful summary of work on an important subject, which has attracted much attention of recent years, and towards which Jeffries has made important contributions. Briefly, it has been found that the recrystallisation temperature is lower the greater the amount of cold work, the lower the temperature of working, the purer the metal, the smaller the grains before deformation, and the longer the time of exposure at the recrystallisation temperature.

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[19] *Metal Ind.*, 1922, April 21.

[20] *Proc. Roy. Soc.*, 1921, **A 100**, 329; *J.*, 1922, 17A.

[21] *Chem. and Met. Eng.*, 1922, **26**, 343, 402.

F. Adcock[22] traces recrystallisation in cupro-nickel (80% Cu, 20% Ni) reduced in thickness without intermediate annealing, approximately 50, 75, 88, and 97%. Recrystallisation commenced in the material reduced 88% at about 450° C. and the hardness fell rapidly on exceeding 460° C.

F. C. Thompson and E. Whitehead[23] find the best annealing ranges for nickel-silvers containing 10–20% of nickel to be between 700° and 800° C.

C. J. Smithells[24] develops the work of Jeffries on the grain growth of tungsten and the effect of mechanically-associated impurities, and advances theories based on the Beilby conception of the amorphous phase in metals. The theories are largely hypothetical, and it is not easy to agree entirely with the author in his conclusions.

J. H. Andrew and R. Higgins[25] give the results of the annealing of a composite specimen prepared by casting a γ-brass on to a thick rod of pure copper. It was found that high temperatures promote both diffusion and grain growth simultaneously, whilst at low temperatures diffusion will not only prevent grain growth, but will actually break down existing grains into smaller units. The second observation is novel and important, and further confirmatory experimental work will be looked forward to with interest. An important suggestion, which, however, remains to be verified, is made, that in annealing castings which possess a cored structure annealing should be stopped just prior to the complete elimination of the cores and before grain growth commences.

The authors do not accept the amorphous cement theory of Rosenhain, and revert to the earlier ideas of imperfect packing of atoms at grain boundaries, so permitting of slight movement of atoms resulting in coalescence of adjacent grains under the right conditions. Their hypothesis is made to account for the precipitation of new phases at the grain boundaries, and for the etching effects observed.

ALLOY SYSTEMS.

L. Guillet[26] discusses the properties of cerium and its alloys with iron, aluminium, magnesium, bismuth, tin, and silicon. With each of these elements cerium forms one or more compounds. The same author has studied alloys of magnesium and cadmium, and finds that two solid solutions are formed which within certain limits of concentration undergo allotropic transformations. The alloys are malleable at ordinary and at high temperatures, and quenching has no influence either on structure or on properties.

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[22] *J. Inst. Metals*, 1922, No. 1., 73; *J.*, 1922, 257A.

[23] *Ibid.*, 1922, No. 1, 227; *J.*, 1922, 256A.

[24] *Ibid.*, 1922, No. 1, 107; *J.*, 1922, 257A.

[25] *Ibid.*, 1922, No. 2, 185; *J.*, 1922, 819A.

[26] *Rev. Mét.*, 1922, **19**, 352.

D. Hanson and M. L. V. Gayler[27] have revised the constitutional diagram for alloys of aluminium and zinc put forward by Rosenhain and Archbutt. They find that the β-constituent obtained by quenching alloys of suitable concentration decomposes spontaneously and rapidly, with the evolution of considerable heat. A similar spontaneous decomposition can probably take place in alloys consisting wholly of the γ-solid solution under suitable conditions. The phenomenon of age-hardening shown by these alloys was made the subject of careful investigation, and curves reproduced show a marked increase in hardness in certain quenched β-alloys over a period of about five minutes after quenching, followed by a less rapid and diminishing rate of softening over a period of about three hours, to a value rather higher than that possessed by the material immediately after quenching. M. L. V. Gayler[28] carries the study of age-hardening a stage farther, and finds in aluminium alloys containing copper and magnesium silicide that it is due to the difference in the solubility of both the compounds $CuAl_2$ and Mg_2Si in solid aluminium at high and low temperatures; of the two Mg_2Si produces the greater amount of age-hardening.

The antimony-bismuth system has been studied by M. Cook,[29] who finds a continuous series of solid solutions. Q. A. Mansuri[30] shows that thallium and arsenic alloy in all proportions, but do not form solid solutions or compounds with one another. The eutectic of the system occurs at the composition 8·01% As, freezing at 215° C.; all alloys containing from 13% to about 40% of arsenic begin to freeze at 240° C., and are made up of two layers, the upper rich in arsenic and the lower rich in thallium. With over 40% of arsenic the two layers merge into one.

C. A. Edwards and A. J. Murphy's[31] experiments lead them to believe that in addition to the phosphide Cu_3P, two phosphides, CuP and Cu_5P_2, exist in the copper-phosphorus system. They determined the rate at which solid copper combines with phosphorus at various temperatures up to 700° C., and found that the maximum rate of increase in phosphorisation for a given rise of temperature was at 640° C.; they express a belief that it is possible to produce commercially at this temperature phosphor copper which will contain more than 15% of phosphorus.

CORROSION OF NON-FERROUS METALS.

The Sixth Report to the Corrosion Research Committee of the Institute of Metals[32] constitutes another valuable contribution to the study of corrosion. Experiments described were confined to the corrosive effects of solutions of the chlorides of copper, zinc, and nickel on copper, zinc, and nickel with free access of air.

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[27] *J. Inst. Metals*, 1922, No. 1, 267; *J.*, 1922, 256A.

[28] *Ibid.*, 1922, No. 2, 213; *J.*, 1922, 818A.

[29] *Ibid.*, 1922, No. 2, 421; *J.*, 1922, 819A.

[30] *Ibid.*, 1922, No. 2, 453; *J.*, 1922, 819A.

[31] *Ibid.*, 1922, No. 1., 183; *J.*, 1922, 257A.

[32] G. D. Bengough and J. M. Stuart, *J. Inst. Metals*, 1922, No. 2, 31; *J.*, 1922, 820A.

The authors believe that no one of the theories of corrosion previously advanced accounts satisfactorily for the effects observed. "Corrosion may be caused by actions of more than one type, and the final condition of the corroded metal may be the end result of a series of complicated phenomena. The initial action may be either chemical or electro-chemical, and may take place in either acid, neutral, or alkaline media; it is by no means dependent solely, or even mainly, on the hydrogen ion concentration. The corrosive properties of a liquid depend on the specific nature of all the ions in solution, as well as on the presence of undissociated substances, of which oxygen is the most important; they are not necessarily proportional to the conductivity of the solution."

The function of oxygen in corrosion receives full attention, and the two views that have been put forward to account for its action are criticised and discussed. The authors appear to lean to the view that the main function of oxygen in corrosion is that of a depolariser.

Discussion of the protective effect of scale leads up to the main thesis that one of the principal factors to be considered in any investigation of corrosion phenomena is the formation of colloids in the liquid. "Two well-defined types of corrosion, differing markedly in their effects on the metal surface, can now be distinguished from one another: (A) All corrosion products, except hydrogen and displaced gas or metals, completely soluble in the corroding liquid, giving true solutions. In such cases the metal surface is comparatively evenly attacked, and the solution tension theory gives a reasonably correct account of the phenomena observed, though a strictly electro-chemical application of it is not necessary. Examples, sodium in water, and zinc in hydrochloric acid. (B) One or more corrosion products comparatively insoluble in the corroding liquid, and closely adherent to the metal surface. Metal surface usually attacked locally, giving isolated 'pits.' ". . . during corrosion of type B the surface of the metal becomes covered initially with products of a colloid and gel nature, and it seems reasonable to suppose that the explanation of the differences between such corrosion and that of type A is to be found in the physics and chemistry of colloids."

The conditions of the stability of colloids, the formation of the gel film and its influence on corrosion, the manner in which the gel protects the metal under certain conditions, how discontinuities in the gel film resulting in local corrosion being developed may be produced, and the action of salt solution on this film are discussed.

OTHER INVESTIGATIONS.

H. Moore and S. Beckinsale[33] consider that treatment of Admiralty condenser tubes at 280°–300° C. for 30 minutes would remove all liability to the development of season cracking, and would at the same time effect a useful improvement of mechanical properties, especially in the harder tubes, by raising the limit of elasticity.

K. Bornemann and F. Sauerwald[34] have determined the volume changes in melting copper, aluminium, tin, and alloys of these metals. Copper shows on melting an expansion of 4·2% of the solid volume, aluminium one of 6·7%. The apparatus employed consisted of a vertical iron tube, water-cooled at the top end and surrounded by an electric furnace at the bottom. A salt mixture was contained in an inner porcelain vessel, and the metal used (8 or 9 c.c.) was introduced in the form of a cylinder inserted in a silica vessel. The loss of weight in the salt bath (the density of which was determined by means of a tungsten sinker) permitted of the determination of the density of the metal or alloy under investigation at any particular temperature. In further papers the systems Cu–Sb, Cu–Zn, Cu–Al, and Sn–Bi are studied.

K. Gilbert[35] has carried out similar work on easily fusible alloys, with a view to determine the volume changes in dental alloys.

Nickel-Chromium Alloys.—Attention has been called during the year to, amongst others, alloys of nickel and chromium practically free from iron (for example, Kromore containing 15% Cr), which are superior to ordinary nichrome metal for use as heating elements in wire-wound electric furnaces. On account of increased resistance to oxidation they may be heated for long periods at 1000°C. without failure.

O. Smalley[36] records the results of a large number of experiments dealing with additions of aluminium, manganese, tin, and iron, separately and together, to brass, and their effects on the physical properties. In spite of the large amount of work which has been carried out in the past, our knowledge of the complex brasses is still very incomplete and this paper represents a valuable contribution to the study of these alloys. A knowledge of the effect of the elements considered is important for they are frequently present in brasses, sometimes by design and sometimes by accident.

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[33] *J. Inst. Metals*, 1922, No. 1, 149; *J.*, 1922, 255A.

[34] *Z. Metallkunde*, 1922, **14**, 145, 254, 329; *J.*, 1922, 421A.

[35] *Ibid.*, 1922, **14**, 245; *J.*, 1922, 553A.

[36] British Foundrymen's Assoc., 1922; *Metal. Ind*, July, 1922, *et seq.* 1922, 761A.

ELECTRO-CHEMICAL AND ELECTRO-METALLURGICAL INDUSTRIES.

By J. N. Pring, M.B.E., D.Sc.,

Research Department, Royal Arsenal, Woolwich.

General.

The general outlook with electro-chemical and electro-metallurgical practice during the last year has improved together with the gradual recovery of chemical and metallurgical industries. Statistics show these industries to have been at their lowest ebb in the middle of 1921, since when a constant improvement is to be noted in all countries, though the normal level of the industry has not yet been reached.

The main advance which has been made recently in electro-chemical processes as applied to metallurgy consists in an extension of methods for the production of metals in a high degree of purity. Such processes are being applied to an increasing extent in the case of copper, zinc, lead, tin, aluminium, iron, nickel, magnesium, antimony, and the rare metals. In the case of copper, 75% to 85% of the world's output is now refined electrolytically to give a metal of 99·9% Cu and permitting of subsequent purification of the accompanying rare metals, silver, gold, platinum, etc. The output of electrolytic zinc, though the process has only been in operation for five years, is estimated at 150,000 tons per annum. Aluminium is now obtained of 99·5% purity, whereas, as obtained formerly, the metal contained 2–3% of impurities. Electrolytic iron, which, on account of its high purity, has unique properties, is at present only produced for special purposes.

The demand for special electric furnace steels and ferro-alloys has increased on account of the progress of the automobile industry. Many electric steel furnaces which were formerly suspended have been brought into operation again and new units installed. The demand for aluminium has increased and an extended application has been made of its alloys.

There is also to be noted, especially in Switzerland, an increase in the production of calcium carbide, which suffered most from the crisis of 1921.

With regard to synthetic fertilisers, the production of calcium nitrate and ammonia by the arc furnace has not developed in countries other than Norway, while the output of cyanamide and its derivatives has not been affected appreciably by the competition of the processes of Haber, Claude, or others.

The trend towards employing electric furnaces for the treatment of non-ferrous metals to an increasing extent is still apparent.

An account of recent progress which has been made in organic electro-chemistry is given by E. K. Strachan.[1] War-time developments have called attention to the great variety of organic chemicals that can be produced from acetylene. These include aldehyde, paraldehyde, alcohol, acetic acid, ethyl acetate, acetone, ethylene, acetonitrile, many chloro derivatives, such as tetrachloroethane and chloroacetic acid, and many other compounds. Under present conditions, most of these products can hardly compete with wood distillation processes, but further research may be expected to make these reactions of considerable commercial importance, particularly as power becomes cheaper and wood for distillation becomes scarcer.

At the present moment the construction of electrochemical works, based on the use of hydro-electric power, remains in abeyance throughout the world on account of the present high costs of water power development in relation to existing installations. Under present conditions a figure of £45–50 per kw. installed, corresponding to 0·3d. per kw.-hr., may be taken as an average price of hydro-electric power from a modern development[2] on the basis of 4000 working hours in the year, while the cost of power from older installations may be taken at from 0·07d. to 0·14d. per kw.-hr.

IRON AND STEEL PRODUCTION.

Electro-thermic Smelting of Iron Ores.

Pig-iron is now being produced in electric furnaces by two distinct methods: (1) By reduction of iron ore with coke or charcoal and electric heat, and (2) the production of synthetic cast-iron or the reconversion of steel scrap into pig-iron or iron castings Sweden, Norway, and Italy have always led in the former, while France and Canada are the main countries to engage in the latter process.

According to A. Helfenstein[3] the importance of electro-therma smelting of iron ores in countries such as Scandinavia, which possess large water powers, has increased in recent years on accoun of the high price of coke. When the process is carried out with an efficient gas recovery plant, the pig-iron made by electric heating may be regarded as a by-product in the production from carbon o a gas of high calorific value to be applied for heating purposes. I the electric smelting process, the consumption of carbon, in th form of charcoal, coke, or anthracite, which is only required for the chemical reduction, is only one-third of that needed in the blast furnace where carbon, by combustion, is required to raise the temperature. With the blast furnace the volume of gas produced amounts to 4000–6000 cub. metres per ton of cast iron of a calorific value of 1000 cals. per cub. m. (112 B.Th.U. per cub. ft.). With the electric furnace, the volume of gas amounts to 600 cub. m. with a calorific value of 2500 cals. per cub. m. The carbon dioxide in the gases ascending the heated charge in the shaft reacts to some extent with carbon to give the monoxide, while more of the monoxide is oxidised to dioxide by reducing the ore. For the purpose of gas recovery it can be arranged to withdraw the gases from the zone where the ratio of monoxide to dioxide is the highest, or alternatively to adjust the height of the charge in the shaft, a limiting value of about 10 feet being found most advantageous. Processes for the electric smelting of iron ores may be divided into two classes according to the use of a high or low column of charge in the shaft. The former type is employed in the furnace of Grönwall, Lindblad and Stalhane, and is suited for use with charcoal as a reducing agent, but offers considerable difficulties with coke on account of the lower permeability of the charge to the gas and the lower resistance, which necessitates the use of larger currents at lower voltages, while the greater density of the charge involves the expenditure of more energy per unit volume. Furnaces with a low column of charge, *i.e.*, from 6 inches to 4 feet, as in the Helfenstein type, are better adapted for use with coke. With the lower column the ratio of carbon monoxide to dioxide is higher and the consumption of carbon and energy expenditure are consequently increased, but the calorific value of the gas is higher. Recent developments with the Helfenstein furnace have been in the automatic charging and adjustment of the height of the charge, the use of continuous electrodes, the increase in the dimensions of the electrodes, and progress in the construction of transformers. The gas produced has been applied to the heating of furnaces in which the cast iron obtained is transformed into steel.

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[1] *J. Ind. Eng. Chem.*, 1922, **14**, 910.

[2] *J. du Four Elec.*, 1922, **31**, 129.

[3] *Ibid.*, 1922, **31**, 45.

An historical account of the development of iron-ore smelting in California is given by R. C. Gosrow.[4] At the works of the Noble Electric Company at Héroult a rectangular type of furnace is at present in use, employing four vertical graphite electrodes in a straight line. With a unit of 2250 kv.a. smelting iron ore, the output amounted to 20 tons of foundry iron daily, corresponding to 2700 kw.-hrs. per ton of pig. Charcoal was used as reducing material and prepared locally. 800 lb. of charcoal was needed per ton of pig-iron. In 1914, the manufacture of pig-iron was replaced by that of ferro-manganese.

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[4] *Chem. and Met. Eng.*, 1922, **27**, 490.

Synthetic Cast Iron.

At a symposium of the American Electro-Chemical Society in April, 1922,[5] a discussion was held on the manufacture of pig-iron in the electric furnace, of synthetic cast-iron from steel scrap or iron turnings, and on the melting of pig-iron by electrical heating and desulphurising of cupola-melted grey iron.

A description is given by W. L. Morrison[6] of experimental work which was carried out on the manufacture of synthetic cast-iron in a 2-ton electric furnace of the stationary type, with a consumption of 750 kw. Rammed silica was found the most suitable lining material for the bottom. A representative charge consisted of 500 lb. of turnings, 50 lb. of anthracite dust, 20 lb. of ferro-silicon (50%), 2 lb. of ferro-manganese (80%), 5 lb. of lime, and 2 lb. of fluorspar. The charge was added continuously and tapping conducted intermittently, while the accumulated slag was removed about every two days. Aluminium carbide is formed at the temperature of the furnace and produces blow-holes and the appearance of burnt iron in the product. The defect can be prevented only by a proper selection of refractories and by excluding dry aluminous slags from the metal. The average analysis of the iron made was 2·25% Si, 3·5% C, 0·65% Mn, 0·004% S, 0·15% P. This work was conducted at Portland, Ore., where grey iron castings are produced from turnings and steel. An account is given of different types of furnaces in use and different methods of carburising and an estimate made of the costs of operation of electric smelting.

An installation in operation at Aarau in Germany, similar to the above, is described by K. Dornhecker,[7] who discusses the thermochemistry and economics of the process. The furnace employed is of the arc type in which the electrodes dip into the upper part of the charge so that heat is generated by resistance as well as by the arc. The furnace charge consists of good quality scrap iron with an excess of coke and sufficient lime. The amount of sulphur in the product is below 0·02% and phosphorus below 0·1%.

A plant which has been in operation since 1917 at Cincinnati, Ohio, for the production of cast-iron and semi-steel from scrap is described by G. K. Elliott.[8] The plant has recently been extended on a larger scale at Birmingham, Ala. The process, which utilises a Héroult type of furnace, is now operated as a duplex system in which a cupola is employed for the initial melting stage, followed by a basic-hearth electric furnace for desulphurising, deoxidising by carbon, silicon, and manganese, reducing the carbon by dilution with steel and adjusting the silicon to suit the size and nature of the castings. A discussion is given of the refining reactions, the effect of oxygen in cast-iron, the advantages of superheat, the influence of oxides of carbon in solution, and the extent to which these factors are modified by electric furnace practice. A furnace in use for the melting of cast iron in a Booth rotating electric furnace is described by H. M. Williams and T. B. Terry.[9] The furnace is lined with "Suprafrax," a high-alumina clay, and the lining lasts for over 200 heats. The furnace is used chiefly for the melting and reclaiming of machine turnings. The practical aspects of electric grey iron production are discussed by C. H. vom Baur.[10] The important advantage of electric treatment over the cupola is that borings and turnings can be used as the charge in the former case. In general practice the charge is pre-heated in a fuel-heated furnace before admitting to the electric furnace.

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[5] *Chem. and Met. Eng.*, 1922, **26**, 820.

[6] *Ibid.*, 1922, **26**, 312 ; *J.*, 1922, 254A.

[7] *Stahl u. Eisen*, 1921, **41**, 1881 ; *J.*, 1922, 103A.

[8] *Chem. and Met. Eng.*, 1922, **27**, 116.

Electrolytic Iron.

The physical properties of electrolytically deposited iron and its commercial possibilities have been summarised by B. Stoughton.[11] The main features are purity, ductility, rust-resisting properties, and high thermal and electrical conductivity, which make the substance suited for boiler tubes, fine iron wire, cold-worked parts of precise shape, and electrical and magnetic specialities. A description is given of the process in operation by the Société "Le Fer" in France.

An account is given by G. F. McMahon[12] of the general arrangement and operation of a commercial plant for the electrolytic refining of iron. The effects of composition, temperature, and circulation of the electrolyte upon the physical properties of the deposited metal are considered. A small amount of glue in the electrolyte is found to be beneficial in the operation of large tanks. An average output of 1·5 lb. of refined iron per kw.-hr. is obtained in practice. The electrolyte employed is ammonium sulphate or chloride together with ferrous sulphate. The solution is generally neutral or very slightly acid or alkaline. It is recommended to filter the electrolyte continuously in order to keep the impurities low. For a high-grade product, the anode iron must be as pure as possible and for most purposes, Bessemer or open-hearth steel may be used. The cathode starting sheets are made from thin steel plates with holes drilled to ensure better adhesion of the deposit. Before use the cathodes should be pickled in dilute sulphuric acid, washed in hot water, and coated with a mineral oil, such as kerosene. A thickness of ¼ inch is obtained after 12 to 13 days' electrolysis, when the deposit is stripped. The solution becomes alkaline during the progress of the electrolysis and is carefully neutralised by the addition of sulphuric or hydrochloric acid. Excess of alkali causes the formation of ferrous hydroxide in the deposit, and slight excess of acid produces a brittle, curly, and mirror-like surface, while a neutral or very slightly alkaline electrolyte gives a good matt grey deposit. An excess of ferrous sulphate increases the tendency to tree formation and low ammonia content leads to excessive gas evolution. A high chloride concentration is, as a rule, beneficial, but if occluded in the metal, leads to rapid corrosion on exposure to the atmosphere. The magnetic permeability of the iron rises with increasing temperature of the electrolyte. It is preferable to work at a temperature of about 45° C. and a current density of 12–15 amps. per sq. foot, when the current efficiency is approximately 90%.

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[9] *Trans. Amer. Electrochem. Soc.*, 1922, 285 ; *J.*, 1922, 466A.

[10] *Iron Age*, 1922, **109**, 51.

[11] *Iron Age*, 1922, **109**, 32 ; *Chem. and Met. Eng.*, 1922, **26**, 128.

[12] *Chem. and Met. Eng.*, 1922, **26**, 639.

A process which has been applied for the electrolytic extraction of iron from pyrrhotite is further described by F. A. Eustis.[13] The procedure consists in grinding the sulphide ore and agitating with spent electrolyte containing ferric chloride when reaction takes place as follows :—

$$2FeCl_3+FeS=3FeCl_2+S.$$

Sulphur and other insoluble matter are then filtered off and the solution is electrolysed in a diaphragm cell with graphite anodes. Iron is deposited in the cathode compartment and the chlorine migrates through the diaphragm to the anode and oxidises ferrous to ferric chloride. The solution in this compartment is circulated to prevent the concentration of iron from exceeding a certain value. The current efficiency in the deposition exceeds 95%. D. R. Kellogg[14] gives details of the procedure recommended for the building up of worn or undersized parts by the electrolytic deposition of iron.

An account of experiments on the influence of heat-treatment in modifying the properties of electro-deposited iron is given by N. R. Pilling.[15] Annealing at 900° C. is found to be necessary to produce complete and rapid softening. The rate of decomposition of the unstable iron-hydrogen compound, which is assumed to be an essential component of electrolytic iron, was observed at different temperatures.

An account is given by R. P. Neville and J. R. Cain[16] of the preparation of an extensive series of very pure alloys of electrolytic iron, carbon, and manganese, which was conducted by melting in an Arsem vacuum furnace.

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[13] *Chem. and Met. Eng.*, 1922, **27**, 684.

[14] Amer. Inst. Min. Met. Eng., Feb., 1922 *J.*, 1922, 330A.

[15] *Chem. and Met. Eng.*, 1922, **27**, 676.

[16] *Ibid.*, 1922, **27**, 677.

Ferro-Alloys.

The types of furnaces now in use for the preparation of ferro-alloys conform to the general principle of possessing a cylindrical receptacle of masonry or metal provided with a refractory lining in the interior of which two or three electrodes are admitted. When using metallic cases, the complete circuit of magnetic metal is interrupted by the insertion of a strip of non-magnetic metal. The majority of ferro-alloy furnaces contain a hearth electrode with one or two electrodes suspended above. The main differences in the different types are in the manner of constructing the base electrode. In some cases this consists of a plate of steel embedded in the lining of anthracite and tar which forms the hearth. In the furnaces at Giffre[17] a series of steel bars are arranged in fan shape, resting on a layer of lining. Other devices are the Keller conducting hearth, a graphite hearth consisting of a large graphite electrode projecting below the base of the furnace or a graphite electrode held in an iron casting provided with water circulation. Important factors in the economy of ferro alloy manufacture are utilisation of the gases evolved partly by re-circulating through the furnaces for the reduction of oxides and the remainder for power and heating purposes. Electrical precipitation and other means of recovering dust are also important on account of the value of the ore, especially in the case of ferro-manganese production. Open-top furnaces have accordingly been replaced in several instances by those with closed tops. Other directions in which recent marked developments are pointed out[18] are in the use of higher temperatures produced by the use of higher current densities, high voltage, and very close electrode spacing. It has become possible to treat lower grade ores at a reasonable cost and, in this way, to lower the prices of several ferro-alloys.

Another direction in which rapid progress has been made in this branch of electro-metallurgy is the refining of ferro-alloys containing large percentages of carbon and silicon, particularly in the case of ferro-chromium in its application to the manufacture of stainless steels. Several processes have recently been devised for the removal of carbon from these alloys.

The development of high-chromium, low-carbon steels has also led to processes for introducing the chromium without the necessity of first manufacturing a ferro-chrome. In such processes the reducing agent, either metallic or non-metallic, is placed in the bath of molten steel, together with the raw chrome ore and suitable fluxes, when the oxide is reduced and the metal alloys with the steel. Another alloy which has gained prominence commercially is ferro-phosphorus. In its manufacture the electric furnace is supplanting the blast-furnace method.

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[17] *J. du Four Elec.*, 1922, **31**, 71.

[18] B. D. Saklatwalla, *J. Ind. Eng. Chem.*, 1922, **14**, 862.

ELECTRIC STEEL FURNACES.

The progress of electric steel manufacture generally has been retarded since the Armistice; this is to be attributed, apart from trade depression, to the temporary large stimulus during the war period, and, in the case of alloy steel plants, to the existence of large stocks of finished bars. Recovery is now to be noted, however, several new plants having been restarted and new ones installed. Statistics by E. F. Cone[19] show that in 1921 the United States was the largest producer of electric steel with an output of 169,499 tons and Italy second with 140,000, while Great Britain produced 27,100 tons.

At the works of Messrs. E. Allen and Co., Sheffield, one 10-ton and one 3½-ton electric steel melting furnaces have been installed and are worked together in a process whereby scrap steel is electrically melted and refined by oxidation in a continuous manner in the large primary furnace, and a third or more of the molten bath is transferred at short intervals to the small secondary furnace for finishing.

In an article on deoxidation and desulphurisation in the Héroult furnace, by F. T. Sisco,[20] it is pointed out that recent developments in electric furnace practice have made it possible to ensure the preparation of steel of any desired chemical composition and within narrow limits of specification. It is considered that electric steel is, as a rule, still decidedly inferior to crucible steel, and that the inferiority is largely due to insufficient knowledge of the proper conditions for deoxidising the metal. A description is given of three procedures by which the highest grade of electric steel is obtained from scrap. In (1) the melting is effected without oxidation. A quantity of limestone is first placed in the furnace giving a white slag, which is formed as soon as molten metal collects around the electrode and remains as a cover for the metal throughout its subsequent treatment. Method (2) consists of melting with partial oxidation and provides the best method where a base of lower quality is used and for steel of moderately high carbon content. The practice consists in placing a layer of limestone on the base of the furnace, admitting a charge of clean scrap which is selected to give a carbon content when melted slightly below the required amount. When the metal is all molten, the slag is removed and immediately replaced by a white slag, which consists of lime, with a small proportion of coke and fluorspar. Some carbide is formed in the slag at this stage. The deoxidation is completed by the addition of ferro-alloys. Method (3) consists of melting with complete oxidation and is employed when a low-carbon product is desired and for the treatment of very low-grade scrap, phosphorus as high as 0·08–0·1% being reduced with ease to below 0·02%. The procedure begins as in the case of the other methods, and iron ore or roll scale is added to the charge. Oxidation is generally complete by the time the metal is melted. The oxidising slag is then removed and the required amount of carbon introduced by adding crushed coke or electrodes to the metal. White slag is then added for a final deoxidising treatment of the metal. The action of this slag is to aid in removing oxides and gases, to reduce the oxides which rise to the surface of the bath, and to eliminate sulphur. The last method of operation is also employed in the duplex system when molten metal is received from the open-hearth furnace in a condition similar to that resulting from the first oxidising treatment described in the above electrical treatment.

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[19] *Iron Age*, 1922, **110**, 683.

[20] *Chem. and Met. Eng.*, 1922, **26**, 17.

Desulphurisation is shown to be brought about by both lime and fluorspar in presence of either carbon or silicon. It is emphasised that, in the past, too great an importance has been attached to desulphurisation, whereas this is considered to be of less consequence than deoxidation.

In an article on the present status of the electric furnace in refining iron and steel by J. A. Mathews,[21] it is pointed out that the reasons for the recent rapid expansion of electrical steel making are the following:—(1) Lowering of cost of power due to hydro-electric and improved steam-plant developments. (2) The extreme flexibility and adaptability of electric furnaces to a wide range of uses. It has been shown by experience that they may successfully be used for melting cold charges or refining liquid charges, for making ingots or castings, and for melting ferro-alloys. They may be used alone, or in conjunction with the Bessemer or open-hearth, and may be operated acid or basic. Other uses are in conjunction with the blast furnace or cupola for making grey-iron, malleable and semi-steel castings. For foundry use particularly the small units are advantageous for making frequent small heats of steel or iron castings. The most popular size of electric furnace in America is of 6 gross tons capacity, but units of from ½ to 40 tons capacity have proved equally successful. In furnaces of 6 tons, or a little larger, hand charging is general, but in the larger sizes, either mechanical charging of cold materials or the use of hot metal charges is usual. Duplexing of open-hearth steel is practised in many of the larger units, while triplexing is done at the large installation of the Illinois Steel Co. (3) Though electric steel is rarely less costly to make than open-hearth metal and never than the Bessemer product, electric furnace steel is in greater demand to meet the new and exacting requirements for ordnance, cars, aeroplanes, and other applications in which alternating stresses occur. The superiority of electric steel is due to the metal being clean and sound or free from oxides and occlusions, while the grain of the steel is more uniform.

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[21] *Chem. and Met. Eng.*, 1922, **27**, 872.

The particular advantages of electric furnace steels have been demonstrated in tests described by W. J. Priestley in a paper on "Effects of sulphur and oxides in ordnance steel."[22] Recent improvements in electric steel furnaces have been confined to mechanical and electrical refinements for improvement in regulation and economy. The more important modifications consisting of automatic electrode regulators, peak load regulators, better-fitting doors, water-cooled arches, better electrodes and holders and economisers to cut down oxidation and waste of the electrodes. No new principles of heating have been employed since the first few years' of furnace practice with the possible exception of the Northrup high-frequency furnace. A modified type of Héroult furnace of 7 tons capacity has been applied at the International Nickel Co. at Huntingdon, W.Va., U.S.A.[23] The furnace is employed for melting and refining Monel metal which is cast into ingots for subsequent forging and rolling. A basic lining is used and desulphurisation and deoxidation are conducted under a basic slag. The life of the electrodes is increased and mechanical charging employed. The current is conducted to the electrodes by means of copper pipes through which water circulates. The transformer room is placed under the furnace platform.

In Italy developments have been made with the Fiat furnace.[24] This type of furnace consists of a cylindrical steel plate shell, suitably reinforced, having a hemispherical bottom lined with refractory material. The whole furnace rests on two special curved rails whereby, by means of two hydraulic pistons, the furnace is made to roll and can be inclined to a varying degree to allow of scorification and pouring. The three openings in the roof of the furnace through which the electrodes pass vertically downwards are fitted with cylindrical water pockets containing a series of insulating rings to prevent the electrodes making contact with the metallic wall. A sealing bell device attached to the electrode ensures that the roof is hermetically sealed around the electrode, thus preventing any escape of gas or flame around the electrode and protecting this from oxidation. The furnace is operated with three-phase current at 130 volts for melting and 75 volts for refining. The melting period lasts for two hours and the refining ½ hr.; 150 pourings of 5000 kg. each can be made without interruption. In continuous operation when treating cold scrap steel, the power expenditure amounts to 640 kw.-hrs. per ton of steel cast, which is calculated to correspond to an efficiency of 78% of the theoretical.

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[22] *Trans. Amer. Inst. Min. Eng.*, 1922, **67**, 317 ; *J.*, 1922, **41**, 330A

[23] *Iron Age*, 1922, **109**, 325.

[24] *Elettrotecnica*, 1922, **9**, 74 ; *Chem. and Met. Eng.*, 1922, **27**, 28 : *Iron Age*, 1922, **110**, 151.

The Fiat furnace was developed during the war on account of the difficulty of obtaining pig-iron and coal. Units of 5–6 tons capacity have been in operation in Turin since 1917. The furnace has been applied to obtain both special steels in small quantities and ordinary steels in large quantities. In a note on the Tagliaferri furnace[25] it is stated that 6-ton units have been in operation since June, 1921. An output of 32 tons per 24 hrs. is obtained with this unit, the melting of each charge lasting from 2½–3 hrs., with an energy consumption of 550–690 kw.-hrs. per ton and an electrode consumption of 5 kg. per ton. In notes on electric furnace operation, C. W. Francis[26] enumerates some of the important features in connexion with basic and acid furnace practice, and in the economy of the electric foundry. The points discussed are the grades of lime necessary, the reduction of phosphorus and sulphur, the production of malleable or grey-iron castings, the use of high and low tap voltages, the charging of basic scrap, the making of new bottoms, tapping and pouring, alloy additions in the furnace, position of furnace and supply bins. In an estimate of the costs of electric steel melting,[27] the chief determining factors are given as power charges, electrodes, and labour. Basic working is of higher cost than acid through the longer duration.

The characteristic features of single-phase electric furnaces are described by H. P. Abel, A. A. Liardet, and W. West.[28] The use of this system is limited to small units on account of the disturbance caused in unbalancing of the three-phase supply system. Constructional details, regulation, electrical efficiency, characteristic features, and power consumption are discussed. The furnace lends itself to the simplest form of construction and considerably higher arc voltages can be employed with it, thus enabling the use of smaller electrodes

It is pointed out by W. J. and S. S. Green[29] that the most important application of electric steel furnaces is for the production of tool steel. The comparative merits of crucible and electric steel are described and the costs and relative advantages of acid and basic bottoms are considered, the latter being generally preferred. For tool steels, cold charges are generally preferred to liquid charges, as open-hearth metal is impoverished by the melting conditions and cannot be restored by a single electric furnace operation. F. T. Sisco describes the process in the Héroult furnace of deoxidation and desulphurisation[30] and the manufacture of chromium ball-bearing steel.[31]

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[25] *J. du Four Elec.*, 1922, **31**, 84.

[26] *Iron Age*, 1922, **110**, 277, 345, 421,

[27] *Ibid.*, 525.

[28] *Foundry Trade J.*, 1922, **25**, 398,

[29] *Iron Age*, 1922, **109**, 201, 999,

FURNACES FOR TREATMENT OF ALLOYS AND NON-FERROUS METALS.

There is at present a notable trend towards the greater application of the electric furnace to the non-ferrous industry. Though this development is of more recent date, it is already relatively more important in the world's production than electric steel furnaces. This progress is mainly due to the important advantages obtained by accurate temperature control which is possible with electric heating. Any considerable lowering in the price of current would lead to a large extension of electric heating for many heat-treating operations.

An outline of the different types of electric furnaces now in commercial operation is given by A. G. Lobley,[32] who discusses the power and load factors of different types of furnaces.

In the United States a considerable extension of the use of electric furnaces for melting brass and other non-ferrous metals has recently been made.[33]

New types of furnaces have been designed by the General Electric Co. of New York. A muffled arc system has been introduced for the melting of brass, bronze, and similar non-ferrous alloys.[34] The principle of this furnace is the provision of a trench which extends along each of opposite sides of a rectangular hearth, separated from it by a carborundum brick wall and containing a carbon cross electrode along the bottom of each trench. The upper surface of each electrode supports two carbon arcing blocks, one near each end. A vertical graphite electrode extends down through the roof above each block. The space in the trench around each cross electrode arcing block and the lower ends of the vertical electrode are filled with small pieces of broken graphite. In operation, an alternating potential of about 60 volts is applied between the two vertical electrodes of each heating element and the current flows across very short arcs, which are practically contact resistances, etween the electrodes and the arcing blocks and through he cross electrode and mass of broken graphite. Heat is enerated both by the flow of current through the contact arcs nd through the cross electrodes and graphite. As the arcs are nuffled or smothered in the broken graphite, this whole mass ecomes heated throughout and serves as a heat source of large rea and comparatively low and uniform temperature. Heat is onducted through the carborundum bridge walls to the metal in ontact with them and is also radiated to the roof, which is constructed so as to reflect it on to the metal on the hearth. The two renches constitute separate single-phase circuits and can be perated either as a single-phase or a two-phase unit, and by use f three-phase to two-phase transformers will draw a balanced load rom a three-phase circuit.

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[30] *Chem. and Met. Eng.*, 1922, **26**, 17.

[31] *Ibid.*, 71.

[32] *Metal Ind.*, 1922, **20**, 322, 343.

[33] *Elec. Rev. and Ind. Eng.*, 1922, **80**, 17, 54.

[34] H. A. Winne, *Trans. Amer. Electrochem. Soc.*, 1921, 263; *Chem. and Met. Eng.*, 1921, **25**, 688.

A further new type of furnace operates on the induction principle and is applied for the melting of non-ferrous metals.[35] The top portion of the furnace consists of a cylindrical chamber resembling an ordinary crucible in which the charge is received, melted, and held for pouring. A charging device and pouring spout are provided. Below this chamber and communicating with it through ports or ducts is another chamber in the form of an annulus encircling a primary winding and one arm of a laminated iron core. The narrow ring of metal in this cylindrical chamber constitutes the secondary of a transformer, and the heat in the furnace is generated by the secondary current which flows around the cylinder when alternating voltage is applied to the primary winding. The unidirectional circulation of metal between the melting chamber and the heating chamber, which is brought about by magnetic repulsion, results in uniform composition and temperature of metal throughout the bath. The Detroit Electric Furnace Co. is supplying several furnaces of this type of 2000 lb. 300 kv.a. capacity for electric brass melting.[36]

A new form of rotating furnace has been recently designed by H. A. Greaves[37] and installed at the works of Messrs. Watson and Co., Sheffield, to the preparation of various alloys. The furnace consists of a steel barrel lined with firebricks and supported on rollers geared to a small motor whereby rotation in either direction can be effected. The necessary heat is furnished by an electric arc generated between two or more electrodes and blown magnetically into a large flame, which allows of an even distribution of heat throughout the furnace. Units for brass-melting are made of capacities of 2 and 5 cwt., the former requiring 50 kv.a. and melting 224 lb. of brass per hour, and the latter 100 kv.a. and melting 500 lb. per hour.

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[35] *Iron Age*, 1922, **110**, 271.
[36] *Foundry Trade J.*, 1922, **26**, 523.
[37] *Ibid.*, 1922, **26**, 366.

A new type of furnace known as the Counterflow Car model has been designed and employed in Philadelphia[38] for the annealing of small grey-iron and steel castings. An annealing temperature of 1450° F. (785° C.) is employed and it is important to ensure accurate temperature control and a uniform source of heat. The heating medium consists of ribbons of nickel-chromium alloy arranged along the sides and connected with a power supply at 240 volts, 2-phase, 60-cycle. The charges circulate in the furnace on cars which are admitted through air locks, and by the counter-flow principle employed, the heat radiated from the outgoing charge serves to pre-heat the incoming charge which moves in the opposite direction. The time of passage of the charge through the furnace is about 11¼ hrs. and the capacity of one unit of 180 kw. is 20 tons of charge per 24 hrs. at 1450° F.

The production of nickel-, chromium- and chrome-nickel steel on the Pacific Coast and their properties and heat treatment are described by J. L. Barton.[39]

A furnace for the production of copper matte by electric smelting has been introduced by J. Westly.[40] The furnace is of the Héroult type but contains a crucible with a flat base which has the appearance of a reverberatory furnace. The electrodes dip in the slag and the matte containing 30–40% Cu collects underneath and is emptied through a tapping hole. The mineral treated is formed of complex sulphides, copper and iron pyrites, and pyrrhotite. Three-phase current is employed at 50 periods and 112–230 volts according to the distance of separation of the electrodes and the resistance of the slag. The consumption of current amounts to 700 kw.-hrs. per ton of mineral treated and that of the electrodes 4 kg. per ton.

Heating with High-Frequency Induction Currents.

A description is given by E. F. Northrup[41] of the principles which apply in heating inductively with currents of frequencies sufficiently high to make the use of iron unnecessary for increasing the magnetic induction. With the practicable voltage of 6600 volts, which has been used for charging the condenser, about 20–25 kw. can be absorbed from the supply in single-phase operation. Under favourable conditions, as much as 70% of the power absorbed from the source is finally delivered as heat to the mass. The method of heating with oscillatory discharges lends itself, however, very well to multi-phase operation. A single discharge gap may be used with three electrodes and a three-phase source of supply. By this means, as much as 75 kw. can be drawn from the supply and over 50 kw. delivered to the mass. Heating is found to proceed effectively, whether the mass acted upon is a continuous solid or an assemblage of small and irregularly-shaped pieces. Non-conducting materials, such as glass, may be fused by placing in a conducting crucible. The design of an electrically-heated forging and heat-treating furnace is described by G. M. Little.[42]

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[38] H. Drever, *Forging and Heat Treat.*, 1922, **8**, 47.

[39] *Iron Age*, 1922, **110**, 784.

[40] *J. du Four Elec.*, 1922, **31**, 36.

[41] *Gen. Elec. Rev.*, 1922, **25**, 656.

A discussion on the generation of electric heat and its application to industrial processes is given by E. F. Collins.[43] The different factors are enumerated, which it is necessary to take into account in applying electrical heating to various manufacturing processes. The considerations include those of a chemical, mechanical, physical, psychological, and economic nature.

A paper on furnace design is given by E. L. Smalley[44] and one on the advantages of industrial electric heating by W. S. Scott.[45]

In a further paper on the economics of electric heat-treating, by E. F. Collins,[46] a comparison is made of the different types of fuel, and data are given to show the relative thermal efficiency and cost of heat developed from electricity and from various fuels. Heat transmission and insulation are discussed and the characteristic features of some of the main electric furnaces in use for the heat treatment of metals are detailed.

ELECTRO-METALLURGY OF ZINC.

Electric Smelting.

The electro-thermal treatment of zinc ores is now in industrial operation only in Scandinavia, where two processes are employed. In the method mainly used in Norway, resistance furnaces are used, and in that in Sweden, arc furnaces. The type of resistance process mainly employed is the Tharaldsen furnace, in which the charge of roasted ore and carbon forms the resistance material for the passage of the current. The condenser is formed of vertical partitions with passages at alternate ends and maintained at a temperature of 500° C. The zinc condensed in the first part of the receiver contains 10% of lead, while further on is obtained a distillate with 98% Zn, then pure zinc and finally zinc with a small amount of cadmium. The condensed metal contains 65% of liquid zinc and 35% of grey and blue powder. With a mineral containing 50% Zn, furnaces of 1000 kw. capacity consume 4 kw.-hrs. per kg. of zinc obtained and give 6 tons of metal daily. With a mineral of 30% Zn, the power consumption is 10 kw.-hrs. per kg. of zinc.[47]

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[42] *Trans. Amer. Soc. Steel Treat.*, 1922, **2**, 228.

[43] *Chem. and Met. Eng.*, 1922, **27**, 679.

[44] *Trans. Amer Electrochem. Soc.*, 1922, **42** (*Advance Copy*).

[45] *Chem. and Met. Eng.*, 1922, **27**, 680.

[46] *Forg. and Heat Treat.*, 1922, **8**, 76.

[47] *J. du Four Elec.*, 1922, **31**, 68.

In the Swedish process as used at Trollhattan, the mineral is roasted so as to reduce but not completely remove the sulphur, and then mixed with coke and fluorspar. On exposing to the action of the arc, oxide of zinc and grey metal are recovered and are submitted to a second treatment to give a metal containing 99·8% Zn. With a mineral containing 30% Zn, the power consumption amounts to 1·2 kw.-yr. (of 300 days) per metric ton of metal or 1·6 kw.-hr. per kg. of zinc. The works at Trollhattan now employs 18,000 h.p.

In America, progress in electro-thermic treatment of zinc has been arrested in favour of electrolytic processes. Experimental work has, however, been conducted on the Fulton process at East St. Louis, U.S.A., and details of design and method of operation of a proposed large-scale plant have been published.[48] A summary is given of the advantages obtained by electro-thermic distillation processes.

Electrolytic Processes.

The conditions necessary for the separation of pure zinc from an impure sulphate electrolyte as practised by the Bunker Hill and Sullivan Mining Company of San Francisco are given by U. C. Tainton[49] and comprise: (1) High current density, which gives a high overvoltage for hydrogen. (2) High acid concentration, which gives a high electrical conductivity. (3) Use of a colloid, such as gelatin, which restrains crystalline growth of the cathode deposit and raises the overvoltage of the impurities. The colloid also gives a diminished interfacial tension at the contact surface of cathode and electrolyte and prevents the hydrogen bubbles from adhering to the cathode. (4) Rapid upward movement of the electrolyte past the cathode surface which usually arises automatically at high current densities. Practical work indicates the optimum conditions to be a free acid concentration of about 250 to 300 grams per litre with a current density of about 100 amps. per sq. foot and the presence of a small quantity of colloid.

The recent situation with electrolytic zinc processes is described by W. R. Ingalls.[50] It is pointed out that the electrolytic process of zinc extraction by roasting the sulphide ore to sulphate and leaching has experienced a good many improvements in details. The washing of the filter cake is better done with reduced loss of soluble zinc. Greater regularity in current efficiency is being obtained, mechanical details are being improved, and the difficulties arising from impurities have been overcome. It is no longer necessary to supply sulphuric acid to the process, but is rather a question of disposing of a surplus. The gases from the blende roasting furnace may also be applied for the manufacture of sulphuric acid where a market exists for the product. A field indicated for improvement consists in the better treatment of the dross that is produced in melting the cathodes. This dross is contaminated with ammonium chloride used in the melting furnace and liquating drum and prevents the material being returned to the electrolytic process.

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[48] C. H. Fulton, *Eng. and Min. J.*, 1922, **114**, 8.

[49] *Chem. and Met. Eng.*, 1922, **26**, 873

[50] *Min. and Met.*, July, 1922, 17.

A *résumé* of electroytic zinc practice is given by J. T. Ellsworth.[51]

Experiments on the influence of impurities on electrolytic zinc in industrial practice have been conducted by G. D. Scholl.[52] It is found that as a general rule, impurities, when present below a certain amount, do not attack the zinc deposit very vigorously during the first 15 or 20 hours of deposition. Impurities are much less active when the cathodes are clean and smooth than when they are rough and pitted, but in these cases the adhesion is much less pronounced. An investigation was made of the individual effect of a number of different metals introduced during electrolysis. Arsenic makes the deposit full of holes; antimony causes such rapid resolution of the deposit that after 30 hours only a skeleton is left on the cathode; cobalt, when present to the extent of only 1 part per million results in the production of fibrous, badly corroded deposits; while nickel gives rise to the formation of large concentric banded corrosion pits and porous deposits. Copper appeared to be the least harmful impurity of the metals added, 1 part in 20,000 only slightly reducing the current efficiency. It was found that the action of the impurities was much retarded by the addition of glue to the electrolyte.

An account of the influence of impurities on the electro-deposition of zinc from sulphate solutions is also given by J. T. Ellsworth.[53] It is found that iron present as an impurity does not deposit but consumes current in being alternately oxidised and reduced. About 0·05 gram per litre is the maximum amount permissible. With cadmium, most of the metal deposits with the zinc and when below a certain concentration is found to be a distinct advantage to the deposit.

A description of processes for the electrolytic extraction of zinc in Italy is given by L. Gambi.[54] Most of the Italian zinc ores are found to be suitable for electrical treatment, the sulphate process giving the best results. Installations for the extraction of zinc by this method were erected in Italy in the years 1915 to 1917 to meet war requirements. A works at San Dalmazzo di Tenola utilises the zinc sulphide ore (blende) of Vallauria. The mineral is roasted at a temperature not exceeding 700° C. and the gas developed utilised for the production of sulphuric acid. The roasted ore is extracted to obtain zinc sulphate, which is then electrolysed. The solution contains initially 80 grams of zinc per litre and electrolysis is continued until the acidity amounts to 8%. The zinc is deposited in the form of sheets 0·6 m. × 0·8 m. and 2–3 mm. thick. In the Pyrenees, further progress has been made at Viviez (Aveyron) at the Société de la Vieille Montagne in the installation of electrolytic zinc processes. 4000 h.p. is being developed from a water power and transmitted 40 miles to Viviez.

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[51] *Eng. and Min. J.*, 1922, **114**, 406.

[52] *Chem. and Met. Eng.*, 1922, **26**, 595; *J.*, 1922, 331A.

[53] *Ibid.*, 1922, **27**, 677.

[54] *Elettrotecnica*, 1922, **9**, 189; *Giorn. Chim. Ind. Appl.*, 1922, **4**, 133; *J.*, 1922, 504A.

In Great Britain, electrolytic zinc is advocated as an economic enterprise by S. Field.[55]

CALCIUM CARBIDE.

The preparation of calcium carbide is at present generally conducted in three-phase furnaces with units which range from 5000 to 6000 kw., though, in some cases, these are as large as 8000–10,000 kw. With smaller units of from 1500 to 3000 kw., single-phrase furnaces are used.

The directions in which future developments in carbide manufacture are to be looked for, as with ferro-alloy furnaces, are in the provision of a dome or covered-in roof as in steel furnaces, economiser of electrodes as in the Stobie furnace, collector for gas, and increase in the height of charge up to five feet above the reaction space instead of about two feet in existing practice. In a furnace of 1000 kw., producing six tons of carbide daily, it is estimated that the calorific power of the carbon monoxide liberated is equivalent to 266 kw. of energy and might be usefully employed in the calcining of electrodes.[56]

CALCIUM CYANAMIDE.

It is estimated that 900,000 tons of cyanamide per annum is now manufactured for agricultural and industrial purposes and of this amount, 500,000 tons is produced in Germany.[57] A quantity of this output is applied directly as a fertiliser and some is converted into ammonium salts. The process of manufacture consists in exposing finely-powdered calcium carbide to a stream of pure dry nitrogen and heating. Reaction begins at a temperature of 700°–800° C. and becomes rapid at 1000° C. The product thus obtained contains 20–21% of nitrogen and 20–22% of free lime.

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[55] *Trans. Faraday Soc.*, 1922, **17**, 400.

[illegible] *u Four Elec.*, 1922, **31**, 107.

[illegible]., 1922, **31**, 57.

A notable installation for the manufacture of cyanamide has been in operation at Buda-Pest since 1917.[58] The power required is developed from steam turbines heated by natural gas, which issues at a pressure of 27 atm. from borings in natural deposits; 1 kw.-hr. is obtained from 35 cubic feet of gas. Nitrogen for the preparation of cyanamide is obtained by the combustion of the natural gas under a boiler. In the cyanamide furnaces, powdered carbide is placed in metal cases with perforated bases and mounted on wagons by which they are conveyed through a furnace 150 feet long, made of iron tubes 10 feet long and 5½ feet diameter. The first two tubes over a length of 20 feet are heated to 800° C., where the reaction commences with a rise of temperature and the material is allowed to remain here for four hours. Gradual cooling takes place in the last four tubes. Nitrogen passes in the direction opposite to that of the charge and is thus preheated. The product contains 80% of $CaCN_2$ with 20% of nitrogen.

A process is in operation at Niagara Falls for the manufacture of cyanide from cyanamide in an electric furnace.[59] In this method, a mixture of calcium cyanamide, salt, and calcium carbide is fed into a large crucible-shaped electric furnace lined with carbon blocks. The furnaces are wide at the top and constricted at the base, having a single centrally-hung graphite electrode 12 inches in diameter, the lower end of which is about 12 in. from the bottom of the crucible, which forms the second terminal for a single-phase current. A tap-hole leads from the extreme bottom of the crucible and is closed with an iron plug on a long rod. The furnace is filled with raw materials to a depth of several feet. A very high current density is employed so that heating of the mixture between the electrode and the bottom of the furnace is extremely rapid. When the current reaches a certain fixed upper limit, corresponding to a known temperature of the fused product inside the furnace, the tap hole is opened and the fused material, containing up to 36% of cyanide, calculated as NaCN, is collected.

A continuous process for the manufacture of calcium cyanamide has been installed at Marignac in France by the Société l'Azote Français.[60] A yield of 85–90% is said to be obtained in the conversion of carbide into cyanamide.

SODIUM.

H. E. Batsford[61] gives an historical account of the development of industrial processes for the production of metallic sodium. The methods reviewed include those of Castner, Acker (in which a molten lead cathode was employed), Carrier (fused salt cell, in which molten lead was used as an intermediate electrode), Darling (using sodium nitrate), and Seward and von Kugelgen (utilising a mixed electrolyte containing fluorides).

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[58] *J. du Four Elec.*, 1922, **31**, 99.

[59] *Chem. and Met. Eng.*, 1922, **27**, 32.

[60] *J. du Four Elec.*, 1921, **30**, 104.

[61] *Chem. and Met. Eng.*, 1922, **26**, 888, 932.

MAGNESIUM.

S. T. Allen[62] describes the process developed in Wolverhampton by the Magnesium Company. Methods consisting of the reduction of magnesia by carbon at high temperatures, and the substitition of magnesium in the fused chloride by sodium, have not been developed to successful commercial processes. The industrial preparation of the metal is limited to the electrolysis of the chloride in a fused state, either alone or with an admixture of potassium and sodium chlorides. The method employed at Wolverhampton is a two-stage process. For the first stage, a cathode of molten lead is employed and an alloy of lead and magnesium obtained. In the second stage, the molten alloy is used as anode with an electrolyte of fused chlorides as in the first stage, while the cathode consists of a large number of narrow steel rods immersed to a short depth in the electrolyte.

Other methods of magnesium recovery have been patented by G. O. Seward,[63] using a fused fluoride bath, and by Ingeberg.[64] Its recovery from salt works residue has also been investigated.[65] A brief review of magnesium recovery processes is given by Vickers.[66]

BORON.

Boron is obtained by the electrolysis of fused boric acid rendered conductive by adding borax, and is employed as a metallurgical reduction agent.[67]

HYDROGEN AND OXYGEN.

The costs of production of hydrogen and oxygen electrolytically under varying conditions are given by W. G. Allen.[68] The utilisation of "off peak" power for the production of these gases in large quantities is advocated. A new type of cell adapted to operate at high current densities is described and present and future possible uses for these gases are enumerated.

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[62] *Electrician*, 1922, **88**, 90.

[63] U.S.P. 1,408,141–2 ; *J.*, 1922, 259A, 299A.

[64] G.P. 319,530.

[65] K. S. Boynton, V. Langford, and J. F. G. Hicks, *J. Ind. Eng. Chem.*, 1922, **14**, 908.

[66] *Brass World*, 1920, **16**, 330.

[67] G. Constant and V. Raisin, E.P. 162,252.

[68] *Trans. Amer. Electrochem. Soc.*, 1922, **39** ; *J.*, 1922, 423A.

PHOSPHORIC ACID.

The manufacture of phosphoric acid in the electric furnace is in operation at Anniston, Ala., U.S.A.,[69] with eight furnaces of a total capacity of 20,000 kw. Power is supplied by the Alabama Power Co. from a hydro-electric plant. The process consists in charging a mixture of phosphate rock, coke as reducing agent, silica rock to flux out the excess of lime present in the ore, and iron turnings to form a ferro-phosphorus alloy. By electrical smelting a ferro-alloy containing 24–25% P is obtained and tapped. A further amount of phosphorus is carried off in the furnace gases and oxidised by the air to the pentoxide. The furnace gases and phosphorus fume are then blown through an electrical precipitator, where a product containing as much as 90% H_3PO_4 is collected.

CALCIUM SILICIDE.

Calcium silicide as manufactured in the electric furnace is being used to an increasing extent as a deoxidiser of steel. On account of the presence of calcium, the material is found to be more efficient than silicon in reducing oxide of iron, and further it is found to remove occluded carbon monoxide to form lime, which rises to the surface slag. The alloy is added in the form of a fine powder to the molten steel, preferably during the pouring operation. The alloy employed has the composition: 60–65% Si, 30–35% Ca, 2–3% Al.[70]

MISCELLANEOUS PRODUCTS.

Many processes have been devised recently for the electrochemical production of chemical compounds and some of these are in successful commercial operation. The products thus obtained include anhydrous aluminium chloride,[71] lead arsenate,[72] chromic acid,[73] potassium ferricyanide,[74] hydrogen peroxide,[75] perborates,[76] perchloric acid by oxidation of hydrochloric acid,[77] and permanganate.[78]

ELECTRO-DEPOSITION.

Considerable attention has been given lately to zinc-plating, which affords better protection than dip galvanizing.[79]

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[69] *Engineer*, 1922, **123**, 688; *Chem. and Met. Eng.*, 1922, **26**, 726; *J. Ind. Eng. Chem.*, 1922, **14**, 630.

[70] *J. du Four Elec.*, 1922, **31**, 44.

[71] U.S P. 1,343,662; *J.*, 1920, 545A.

[72] H. V. Tartar and G. G. Grant, *J. Ind. Eng. Chem.*, 1922, **14**, 311.

[73] R. H. McKee and S. T. Leo, *ibid.*, 1920, **12**, 16.

[74] O. W. Brown, M. Hanke, and I. L. Miller, *J. Phys. Chem.*, 1920, **24**, 230.

[75] F. W. Skirrow and E R. Stein, *Trans. Amer. Electrochem. Soc.*, 1920, **38**, 209.

[76] P. C. Alsgaard, *ibid.*, 1921, **40**, 173.

[77] H. M. Goodwin and E. C. Walker, *Chem. and Met. Eng.*, 1921, **25**, 1093.

[78] *J. Ind. Eng. Chem.*, 1921, **13**, 763.

[79] W. G. Horsch and T. Fuwa, *Trans. Amer. Electrochem. Soc.*, 1922, **41**, 211: *J.*, 1922, 421A.

It is found that cadmium plating on iron is effective in preventing rusting.[80] A process for building up worn metal parts by electrodeposition is described by W. E. Hughes.[81] In this method, worn or undergauged mechanical parts are coated with a layer of metal which is generally iron, though copper and nickel have also been used.

ELECTRODES.

A detailed article on the manufacture, properties, and use of carbon electrodes is given by C. L. Mantell.[82] The historical developments are traced beginning with a description of the charcoal electrodes employed by Davy in 1800. The commercial production of carbon electrodes, mainly for the purpose of arc lamp electrodes, was first achieved by Carré in 1877 by a method in which, as essentially in present-day manufacture, a mixture of finely-powdered coke, lampblack, and sugar solution was kneaded so as to form a thick paste, then pressed through a draw-plate by a hydraulic press, and the extruded carbons baked at a high temperature in retorts. The main lines on which the carbon electrode industry has since developed are in the following applications: (1) Electric arc lighting. (2) Electrolytic manufacture, *e.g.*, of alkali, chlorine, aluminium, and magnesium. (3) Electrothermic work, *e.g.*, calcium carbide, carborundum, graphite, etc. (4) Electric furnaces, *e.g.*, electric steel, ferro-alloys. The most recent progress in electrode manufacture has been in the direction of much stricter specifications as to purity, resistivity, hardness, and increased density of electrodes. The earlier workers attempted to obtain higher densities by saturating the baked articles with binders and baking a second time. At present the end is achieved by employing raw materials of high density and regulating the calcining. The most difficult feature is to achieve uniformity of product. The growth of the manufacture of carbon electrodes in the last 20 years is given in the statement that in 1899 the total value of electric furnace carbon was £2000, while in 1921 this amounted to £2,000,000.

A review is given of the physical and chemical properties of the carbonaceous substances and binding materials from the standpoint of electrode requirements. Electrodes for electro-thermic work usually have high resistivity, and a high ash content is generally unimportant since, as in calcium carbide and steel furnaces, impurities from the electrode are either decomposed or eliminated by the slag. In electrolytic work it is important that the electrodes possess a high degree of purity and low resistivity to avoid contamination of the product and on account of the lower voltage of operation. For large moulded electrodes for electric furnaces, anthracite coal is mainly used. Unless the ash content is low, the coal is generally heated by calcining in a gas oven to remove gas which is burnt under the grate, and then digesting the ground product in a hot concentrated solution of sodium hydroxide, followed by washing in a more dilute solution. Petroleum coke, which consists of the residue from the distillation of petroleum oil by the intermittent process, is mainly used for the manufacture of graphite electrodes by graphitising in an electric furnace. Coke from bituminous coal is used to a considerable extent in Europe for electrodes for electrothermic work. Retort carbon is used only to a small extent for electrode manufacture on account of the limited supplies available. Butt ends or unconsumed or waste portions of finished electrodes are utilised for the preparation of new electrodes by mixing with petroleum coke.

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[80] Knox, *Metal. Ind.*, 1920, **18**, 556.

[81] *Chem. and Met. Eng.*, 1922, **26**, 267.

[82] *Ibid.*, 1922, **27**, 109, 161, 205, 258, 312, 353; *J.*, 1922, 718A, 767A.

A mixture of pitch with a small proportion of tar is generally used as the binding material and is selected to be of a viscosity, which will enable subsequent extrusion of the carbon paste. Too large a proportion of tar produces porosity through volatilisation during the baking process. The condition which is desired in making a carbon mix is to cover each granule with as thin a film of binder as possible, so that when the various particles come in contact they will be well bonded together. For the shaping of electrodes, the material from the mixer is subjected to either a moulding or an extrusion treatment. The moulding process usually results in an electrode of higher density. Small electrodes and those for electrolytic work are usually made by extrusion, while large electrodes are made by both methods, those made by moulding being preferred because of their higher density. Extrusion presses now made enable the production of electrodes as large as 36 inches diameter. The pressures generally employed range from 1200 to 7000 lb. per sq. in., though in some cases, these are said to amount to 25,000 lb.

After extrusion, the electrodes are cut to length and transported to the baking furnaces. These furnaces are generally of the gas-heated type and consist of an enclosed chamber in which the electrodes are closely packed with an intervening layer of finely-divided carbon between each electrode. The chamber is completely filled by means of fine carbon, sealed and heated by surrounding flues in which are circulated the gases resulting from the combustion of mixtures of producer gas and pre-heated air. The temperature is gradually raised to a maximum, which may be as high as 1400° C., and then allowed to cool. During this process the pitch or binding material is decomposed, producing coke, which cements together the granules of carbon. In some cases, electric furnaces of the type of the Acheson furnace are used for the baking process. The surface of the carbons is then cleaned by submitting to the action of rotating steel brushes and finally machined in cases where threads or other attachments are required.

A detailed account of the self-baking continuous electrode is given by C. W. Soderberg.[83] With this system, the ordinary electrode mixture is tamped in a cylindrical case of sheet metal with its lower end at a distance of several feet above the furnace. The casing serves as a mould for shaping the electrode and as a support for the material during baking, and helps to carry the current from the electrode holder to the baked part of the electrode, which projects downwards into the smelting furnace. The material is baked during its descent by means of the heat from the furnace crater and by heat developed in the electrode itself through the passage of the current. The electrode holder is water-cooled, usually placed on the lower part of the electrode and suspended in a frame which may be moved up and down by means of a winch. Movement of the electrode in the holder is carried out by loosening screws on the holder until the electrode will sink by its own weight, and the screws are afterwards tightened. This operation is carried out without interruption of the current, the circuit being always maintained by means of the sliding contact between the electrode holder and the electrode. Fresh mixture is admitted at the top so as to maintain a continuous column. This type of electrode has been applied to furnaces for ferro-alloys, calcium carbide, iron-ore smelting and steel. Electrodes of a diameter of 39 inches are employed in a 6000 kw. three-phase carbide furnace at Knapsack, Alegne. The main advantages of this system of electrode are the marked gain in economy in their preparation, the avoidance of interruption of operation, which is involved by the replacing of electrodes, the avoidance of butt ends, and overcoming the limitation in size, which applies to the usual electrode systems.

A. T. Hinckley[84] gives a review of the uses of carbon electrodes from 1800 to the present time and deals with their application in electric furnaces. The results of a research on the properties of natural and artificial graphites are given by K. Arndt and F. Korner.[85] The specific resistance of rods pressed from different varieties of natural and artificial graphites was determined. The resistance increases with increasing ash content and decreases with increasing size of grain. A determination was made of the resistance of a number of mixtures of graphite and manganese dioxide, such as are used in battery anodes. The addition of this oxide is found to increase the resistance very slightly up to a content of 50–60%, after which a rapid increase is observed.

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[83] *Chem. and Met. Eng.*, 1922, **26**, 1178.
[84] *Elec. World*, 1921, **78**, 1263.
[85] *Z. angew. Chem.*, 1922, **35**, 440 ; *J.*, 1922, 718A.

ELECTRICAL PRECIPITATION OF SUSPENDED MATTER.

In an historical *résumé* [86] of the development of industrial methods for precipitating dust and fume, H. J. Bush points out that this process was first successfully applied to commercial processes by F. G. Cottrell in California in 1906. In the electrical precipitation of liquids and solids from gases as developed technically, a strong electrical field is established by connecting one set of electrodes to a source of high-tension potential, and the other set to earth, the air gap between the two sets of electrodes forming a link in the circuit. The electrodes are shaped to meet the particular requirements and may either be earthed plates opposed by charged wires between which the gas to be cleaned is led, or they may be earthed pipes with charged wires suspended in them, the gas travelling through the pipes and depositing the particles on the inner walls. Precipitation is caused by a number of factors, *e.g.*: (1) Polarisation of the electric charges on the solid or liquid particle carried along by the gas current tending to drive the particle towards the charged electrode. (2) Charge acquired by bombardment of the particle by ions produced in the gas by the corona discharge of the wire electrode. This will impart to the particle a charge impelling it towards the earthed electrode. (3) Transport by electric wind from the discharge electrode. Gases which are highly ionised as when derived from certain metallurgical operations offer considerable difficulties to successful precipitation as the potential difference which can be maintained without disruptive discharge, does not suffice to establish the required electrical field. Electrical precipitation is now in use mainly in the following applications: the condensation of sulphur trioxide fumes in sulphuric acid concentration, the removal of solid particles from blast-furnace gases, the cleaning of roaster gases from pyrites furnaces, and the settling of fumes from lead-smelting furnaces, tin furnaces, alumina calcining, etc. Recent progress in electrical precipitation is described by E. Anderson,[87] who points out that the different types of electrical precipitators in use at the present time are distinguished by the kind of collecting electrode used and are limited to the so-called plate, pipe, and transverse screen treaters. The ordinary precipitator is described as an arrangement of two electrodes of the point-to-plate type with a unidirectional P.D. established between them, of sufficient magnitude to cause ionisation of the gas at the point or discharge electrode. Any solid particles present act as condensing surfaces for the free ions and are transported with these to the collecting electrode. It is found that the rate of precipitation is increased by the presence of water vapour, which is attributed to the prevention of formation of an insulating layer by the particles on the surface of the collecting electrode.

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[86] *J.*, 1922, 21T.

[87] *Chem. and Met. Eng.*, 1922, **26**, 151 ; *J.*, 1922, 180A.

The Cottrell process of electrical precipitation is described by H. A. Winne,[88] who discusses the theory of the process and the operation and construction of different types of precipitators.

R. B. Rathburn[89] gives an account of the metallurgical considerations and treater design in the electrical precipitation of solids from smelter gases and the conditioning of the gas.

N. J. Hansen[90] describes the installation in operation at the Duquesne Reduction Company, Pittsburg, U.S.A., for the recovery of fume from furnaces treating tin ore and drosses. The precipitator is of the pipe type and recovers 2600 lb. of solid from gases emanating from furnaces treating a total of 20 tons of tin drosses daily.

N. H. Gellert[91] discusses the difficulties encountered in the problem of cleaning blast-furnace gas. A description is given of the various features of an electrical precipitation plant and the method of making the gas measurements necessary to determine the required capacity of the clearing equipment.

L. F. Hawley and H. M. Pier[92] describe small-scale experiments, which have shown that it is possible to precipitate the tar electrically from the hot vapours evolved in the wood distillation process.

Generation of Steam by Electricity.

The generation of steam from electricity is finding an increasing application as a means of utilising hydro-electric power when not required for other purposes. There are now more than 300 installations in Italy, Switzerland, Sweden, and France and a few have recently been in operation in Canada and the United States. The methods employed consist in passing an electric current through a resistance, either of metal, consisting of some high-resistance alloy in the form of wire or ribbon or else by passing a current through the water to be evaporated by means of a system of stationary electrodes partly submerged. One kw.-hr. will, in theory, produce 3·17 lb. of steam beginning with water at 150° F., and the heat losses are very small. Within the last two years, generators have been constructed of 2000 kw. or more capacity.[93] A description of the development and present position of electric steam generators is also given by H. Drever.[94]

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[88] *Gen. Elec. Rev.*, 1921, **24**, 910.

[89] *J. Amer. Inst. Elec. Eng.*, 1922, **41**, 676.

[90] *Gen. Elec. Rev.*, 1921, **24**, 1004.

[91] *Ibid.*, 1922, **25**, 428.

[92] *Chem. and Met. Eng.*, 1922, **26**, 1031.

[93] F. T. Kaelin, *J.*, 1922, 412R.

[94] *J. Ind. Eng. Chem.*, 1922, **14**, 923.

OILS, FATS, AND WAXES.

By John Allan,

Messrs. Joseph Crosfield and Sons, Ltd., Warrington.

It has been a very general opinion that the world's consumption of margarine would be largely increased by the greatly enhanced appreciation of its value as a foodstuff, arising from the experience gained of it during the war years, when it was so largely and practically compulsorily used as a foodstuff. There can be no doubt, however, that butter is still esteemed as the prime fatty food for man, and that even a large difference in price between it and its substitutes is no very appreciable aid to the increased consumption of the latter products. It is well known that our factories are working, in total, to little more than one-third of their maximum output, and that the same condition exists both on the Continent and in the United States. Recently issued United States Government statistics show that during the financial year ending June 30th, 1922, only 83,881 tons of margarine was produced in that country, as compared with over 125,000 tons produced in 1921, a decrease of no less than 33%. It has been asserted frequently that large quantities of maize and soya bean oils are used by American margarine manufacturers, but the statistics of the Commissioner of Inland Revenue clearly show that this is not the case, since in 1921 maize and soya bean oils formed only 0·4% and 0·2%, respectively, of the total fats employed.

In this report for last year attention was called to the extraordinary change which had taken place in the sources of supply of various oil seeds, and especially with regard to our imports of linseed and cottonseed from India.

From the point of view of Imperial commerce it is gratifying to find that though our total import of linseed for eleven months of the year is lower than that of 1921 by no less than 110,000 tons, we have received from India over 140,000 tons, as against only 36,000 tons in the same period of 1921. There is little doubt that the absence of Russia as a producer is having a large effect upon the market for linseed. This is in considerable measure compensated for by an increased output from the Argentine, where it is estimated that a record crop of 1,500,000 tons will be available this year. This output, along with an increased internal production in the United States of no less than 300,000 tons, should make for lower prices and larger consumption in this country.

The amount of cottonseed imported from India in 1922 was almost four times as great as that received in 1921, but much more is available from that source, and it is to be regretted that transport conditions in the country of its origin are probably the prime reason for so small a proportion of the actual production being utilised as a source of one of our most valuable oils.

As a possible, but very largely unworked, source of oil there is probably no greater in the world than that provided by the immense forests of *Butyrospermum Parkii*, which stretch behind the oil-palm belt in West Africa. In the form of shea butter the fat from the seeds of this tree is quite largely used in native cooking, and occasional shipments of both seeds and fat are made to Europe. Its use, however, has been limited by the peculiar rubber-like odour of the fat, and still more by the presence in it of a very variable and frequently large amount of unsaponifiable matter (up to 10%). There is some reason for assuming that the amount of unsaponifiable matter is governed either by variety in the species of the trees, or by climatic or other conditions governing their growth. It is interesting to find that the Agricultural Departments of the West African Colonies are investigating the many problems which present themselves in connexion with this product. Work has already been begun in Nigeria, and a report from the Gold Coast Colony,[1] which states that shea trees now existing in that country are capable of producing 260,000 tons of butter annually, indicates that preliminaries for carrying out this work are now well advanced.

The development of coconut plantations on the communal system in the Gold Coast Colony will also be watched with much interest. That copra can be produced there is of course well known, and the success of this experiment seems assured if the phenomenal success of cacao-growing in the country is to be taken as a guide. The plantations now begun are expected to be in full bearing about 1935, but copra will, of course, be produced before that time.

Besides the above evidences of keen Governmental interest in the oils and fats industries, and those remarked upon last year, it now appears that the Brazilian Government[2] is so far interested in the oil-seed possibilities of the country that, after having had a complete survey of the northern part of the country made, it is recommended by the Department concerned that experimental stations be established at Para and Bahia. After a survey of the southern states is completed, it is probable that similar stations will be established in that area.

Our knowledge of the occurrence of the fat-soluble vitamin A in vegetable oils and their raw materials has been greatly advanced by the work of J. C. Drummond and S. S. Zilva.[3] The low value of the majority of vegetable oils as sources of vitamin A has already been established and this fact has been attributed to the treatment to which they are subjected either during extraction or subsequent refining processes. It has now been shown that in the case of a large number of oilseeds practically all of the vitamin A which they contain passes into the oil when it is extracted from them. Linseed, which contains more than the average amount of the vitamin, is an exception to this, as the oil apparently does not contain all the vitamin present. It has not been investigated yet whether this is due to incomplete extraction or to loss by oxidative changes. The growth-promoting activity of palm oil is another striking example of the association of vitamin A with natural colouring matters, and although this association theory has been shown not to be generally applicable it is very frequently true of products of vegetable origin. Isolation of the unsaponifiable matter of palm oil which carried with it the growth-promoting principle proved unsatisfactory, since the product possessed to a marked extent the characteristic odour and taste of the original oil, and on this account would be an unsatisfactory material to use for enriching other oils. Palm-kernel oil, on the other hand, was found to have the low value common to other vegetable oils. The contrast between fats of animal origin and the vegetable oils has been, in large measure, explained by the fact that the chief controlling factor which determines the amount of vitamin A in the former is apparently the amount of that substance present in the diet which the animal has been consuming. The work of J. Hjort[4] and J. C. Drummond and his co-workers,[5] has indicated that the high growth-promoting activity of the fish liver oils is to be attributed to the food consumed by the fish, since marine algæ, diatoms, shrimps, and small fishes which constitute the food of the larger fish are all rich in the vitamin. Indeed, it has been shown[6] that the marine diatom *Nitzschia closterium* is able to synthesise large amounts of vitamin A when grown in sterilised sea-water.

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[1] *Bull. Imp. Inst.*, 1922, 20, 313.

[2] *Cotton Oil Press*, 1922, 5, [11]; *J.*, 1922, 374R.

GENERAL CHEMISTRY.

The preparation of fatty acids from hydrocarbons still receives a great deal of attention, but little progress is indicated in the pub, lished details of the work. Much of this is in the form of patent specifications which cover processss for the preparation of mixtures, more or less suitable for use in the manufacture of soap, the raw materials being usually hydrocarbon residues or tars. Some of these processes are of a most elaborate nature, and seem of very doubtful commercial utility. Thus in a patent granted to C. Harries,[7] highly unsaturated compounds are removed from lignite tar oils by treatment with liquid sulphur dioxide. The residual paraffins and aliphatic compounds with a double linking are separated, the paraffins by freezing, and the unsaturated compounds by steam distillation. A special fraction is treated with ozone, hydrolysed with steam, digested with caustic potash, and heated with superheated steam. Evaporation *in vacuo*, still with superheated steam, then follows, and ultimately potassium palmitate and stearate are obtained. No yields are given, and one cannot help wondering if the process is meant to be taken seriously. H. Siebeneck,[8] without attempting to distinguish the individual products of the reactions which take place, has investigated the oxidation of paraffin wax by means of air or oxygen at a temperature of about 135° C. Products of cracking were found in the early part of the experiments, but later, wax-like products were produced, the quantity of which, apparently, increased up to about 33 hrs.' heating. Thereafter, the ester value, which has increased to an extent equivalent to 70% of esterified acids, fell to 49·16, a change which was accompanied by a very appreciable slowing of the reaction and an increase in viscosity of the products to about five times the original value. The procedure patented by Traun's Forschungslaboratorium G.m.b.H.[9] is similar to many already suggested, in that the oxidation is assisted by catalysts, such as lead or barium peroxide which are employed in presence of an alkali, and the operation is carried out under a pressure of several atmospheres. Except for the provisional use of the suggested catalysts it is difficult to see wherein this process differs from the original process of Schaal,[10] who has apparently anticipated most of these air oxidation patents.

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[3] *J.*, 1922, 125T.

[4] *Ibid.*, 1922, 216R.

[5] *Biochem. J.*, 1922, **16**, 482 ; *J.*, 1922, 913A.

[6] *Proc. Roy. Soc.*, 1922, **B93**, 440 ; *J.*, 1922 564A.

A. H. Salway and P. N. Williams,[11] who have investigated the catalytic oxidation of hexadecane by means of oxygen in presence of 2% of manganese stearate, clearly prove that the result of such-like oxidation processes is to produce compounds which are as readily oxidised as the substances they produce. They suggest that the paraffin hydrocarbon is probably first converted into a fatty acid, which is then further attacked at several points in the carbon chain, with the ultimate production of a complex mixture of monocarboxylic acids of the fatty series, dicarboxylic acids of the malonic series, together with lactones, lactonic acids, formic acid, and carbon dioxide.

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[7] G.P. 339,562 ; *J.*, 1922, 35A.

[8] *Petroleum*, 1922, **18**, 281, 1193 ; *J.*, 1922, 282A, 888A.

[9] E.P. 156,141 ; *J.*, 1922, 425A.

[10] *J.*, 1885, 679.

[11] *Chem. Soc. Trans.*, 1922, **121**, 1343 ; *J.*, 1922, 719A.

The limited appreciation which we have of the causes of rancidity in fats and oils is further emphasised by the work of J. A. Emery and R. R. Henley[12] on the influence of air, light, and metals on its development. The accelerating effect of metals, amongst which iron is included, is pronounced in presence of air or oxygen, but whilst light is necessary for the production of rancidity in absence of metals, it is not essential for the development of rancidity if metals are present. In the dark, if air be excluded, no rancidity will develop, even in presence of metals, but rancidity begins if the air is replaced by carbon dioxide. Moisture, frequently assumed to be a provocant towards rancidity, is found to have little influence in this direction. This work is in several points at variance with that of R. H. Kerr,[13] which was commented upon in the last report.

The interesting work of B. H. Nicolet and H. L. Cox[14] on the structure of linolic acid has led them to the conclusion that only two of the four possible stereoisomeric linolic acids occur, at least in important amounts, in linolic acid as usually prepared, these being the trans-trans and trans-cis forms. As the linolic acid examined was regenerated from the tetrabromide prepared from the fatty acids of cottonseed oil, and recognising the possibility of change during this preparation, it cannot yet be finally assumed that the structure of the linolic acid in this oil has been proved. Using the anilides of the acids as a means of characterising them, the same authors[15] have shown that there is no cis-trans isomerisation when the bromides of oleic and elaidic acids are reduced; in this respect they differ from the linolic acid examined. Clupanodonic acid, to which the odour of fish oils is probably due, is stated by M. Tsujimoto[16] to have the formula $C_{22}H_{34}O_2$, and not $C_{18}H_{28}O_2$, as ordinarily accepted. The acid has been obtained almost pure by fractionating the methyl esters obtained from the highly-unsaturated acids prepared from Japanese sardine oil by the lithium-salt acetone method. The acid had the following characteristics:—sp. gr. 0·9398 at 15°/4° C.; neutralisation value, 172·5: iodine value (Wijs) 300, $n_D^{15}=1·5040$. It is one of the most widely distributed compounds in nature, since it occurs in the fat of all fresh and salt water fish, reptiles, and amphibious animals.

DRYING OILS.

A large amount of work yet remains to be done before our knowledge of the reactions involved in the drying of oils is complete, but we are carried several steps towards this end by the continued work upon the subject of S. Coffey[17] and P. Slansky.[18] It has been already established that the drying of linseed oil can be divided into two stages, an induction period which covers a considerable portion of the total time required for complete oxygen absorption, and a second stage in which the oil, having gelatinised rapidly, passes to its point of maximum oxidation. It has generally been accepted that the increased rate of oxygen absorption which results from the presence of "driers" such as the compounds of lead, manganese, cobalt, etc. in the oil has resulted merely from a speeding up of these processes, but the recent work of Coffey has established the fact that the induction period is so far reduced as to be almost eliminated, whilst the rate of the main oxidation is unaltered. This undoubtedly provides an explanation of the accelerating effect of a drier from the point of view of time, but until it is proved that the resulting "dried" products are the same it cannot be assumed that the course of the oxidation is identical in both cases. Coffey's results strongly support this view, and are corroborated in considerable measure by the previous work of R. S. Morrell.[19] It would certainly appear that in presence of a drier the oxidation of linolic acid is restricted to the absorption of one molecule of oxygen instead of two, and there is probably a similar but more indefinite action in the case of linolenic acid Such effects as this readily explain the fact that in every case the oxygen absorption recorded is lower than that observed when no drier is present, and the reaction curves are different. The bearing of this upon the technical applications of raw and boiled linseed oil is at once evident, since with different reactions dissimilar products almost necessarily result.

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[12] *J Ind. Eng. Chem.*, 1922, **14**, 937; *J.*, 1922, 945A.

[13] *Cotton Oil Press*, July, 1921, 45.

[14] *J. Amer. Chem. Soc.*, 1922, **44**, 144; *J.*, 1922, 259A.

[15] *Ibid.*, 1921, **43**, 2122; *J.*, 1922, 109A.

[16] *Chem. Umschau*, 1922, **29**, 261; *J.*, 1922, 719A.

Slansky[20] has observed the fact that the fatty acids obtained from linseed oil absorb oxygen more rapidly than does linseed oil itself. The rate of oxidation of the oil is increased by the addition to it of linolic or linolenic acid.

The fact that about 35,000 tons of Chinese wood oil has been imported into the United States during this year makes it quite clear that this oil is now extensively used as a substitute for, or in partial replacement of, linseed oil. It is well known that the oil is obtained from various members of the *Aleurites* family, the *A. fordii* being most largely used in China whilst in Japan it is most largely prepared from *A. cordata*. H. A. Gardner and A. Reilly,[21] who have prepared and examined the oil from the seed of *A. cordata*, have clearly established the fact that the two oils are distinctly different, this being made evident by the fact that whereas the oil from *A. fordii* gelatinises on being heated, that from *A. cordata* yields a viscous liquid only. It has frequently been raised as an objection to the use of wood oil that the dried film which it yields is cloudy or opalescent, but this difficulty can be overcome by suitable preliminary heat treatment, whether the oil is to be used in presence of a drier or not. As both varieties of *Aleurites* occur in China and Japan it is highly probable that the imported oil is of mixed origin, and much of the published work on its composition is consequently of limited value. It is known, however, that China wood oil contains a large proportion of α-elæostearic acid, which is readily transformed into the β form when ordinary isolation methods are employed. The work of R. S. Morrell[22] on this acid has been in large measure confirmed by K. H. Bauer and K. Herberts,[23] but until the properties of the two forms of the acid have been clearly established by careful examination of pure specimens, any explanation of the peculiar properties of the oil is largely speculative.

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[17] *Chem. Soc. Trans.*, 1922, **121**, 17 ; *J.*, 1922, 182A.

[18] *Z. angew. Chem.*, 1922, **35**, 389 ; *J.*, 1922, 904A.

[19] *J.*, 1920, 153T.

[20] *Z. angew. Chem.*, 1922, **35**, 389 ; *J.*, 1922, 904A.

[21] *Circ.* **138**, *U.S. Paint Manufacturers' Assoc.* ; *J.*, 1922, 904A.

The extending use of perilla oil, usually in admixture with linseed oil, lends interest to the results of the investigation of the fatty acids of the oil by K. H. Bauer.[24] These are stated to be a mixture of 12% of solid acids, mainly palmitic acid, and 88% of liquid acids which apparently consist of a linolic acid and several geometrically isomeric linolenic acids.

A. Howard and J. S. Remington[25] report on the investigation of a sample of safflower oil prepared by extraction on the semi-technical scale. A yield of 20·6% was obtained, and as the residual meal contained only 2·2% of oil it would appear that the difficulties met with in obtaining satisfactory yields when the crushed seed is hydraulically pressed, and which arise from the high content of fibre, are not extended to the solvent extraction process. The characters of the extracted oil are generally in agreement with those already ascribed to this oil, but the glycerol percentage of 4·6 found by the authors cannot be reconciled with a saponification value of 197·3 and acid value 9·78, unless the oil has a most unusual composition.

It is interesting to note that L. E. Fisher,[26] who has examined two small cargoes of rubber seed shipped from the Malay States to Shanghai, supports the opinion expressed in the Annual Reports for 1920, that the seeds deteriorate so rapidly that it would appear to be advisable to crush them in the country of origin.

SEMI-DRYING AND NON-DRYING OILS.

The fluorescence frequently exhibited by cottonseed oil expressed from seed of Indian and Chinese origin is undoubtedly to be attributed to some constituent of the seed, the presence of which is largely affected by climatic conditions during growth or harvesting. This opinion is upheld by L. E. Fisher,[27] who states that under similar conditions of manuring and cultivation, seed from the same district will one year give an oil with a very evident fluorescence, whereas another year the oil will be practically free from fluorescence. In referring to the suggestion by R. H. Fash[28] that fluorescence can originate from the overheating of crushed seed in the kettle, Fisher states that seed which is badly overheated during storage certainly gives this fluorescence in a more marked degree than fresh seed from the same district; on the other hand, fresh seed from one district may be similar in this respect to over-heated seed from another district. As fluorescent oil gives unsatisfactory results in the refining process, and is therefore depreciated in value as a foodstuff, it would appear to be desirable to ascertain the nature of the fluorescent substance, and establish means either to prevent its development in the seed, or to remove it from the refined oil. With the extension of cotton-growing in our Colonies this defect in oils of Eastern origin is the more worthy of attention.

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[22] *J.*, 1918, 181T.

[23] *Chem. Umschau*, 1922, **29**, 229; *J.*, 1922, 638A.

[24] *Farben-Zeit.*, 1922, **27**, 2756; *J.*, 1922, 719A.

[25] *Bull.* 124, *Agric. Res. Inst. Pusa*, 1921; *J.*, 1922, 109A.

[26] *Cotton Oil Press*. 1922, **5**, [12], 36.

Since the large quantities of grape-seeds which are available in wine-producing districts are a potential source of oil, its approximate composition as determined by F. Rabak[29] is of interest—linolin, 53·6; olein, 35·9; palmitin, 5·2; stearin, 2·2; unsaponifiable, 1·6%.

The detailed analysis of maize oil carried out by W. F. Baughman and G. S. Jamieson[30] has cleared up several points which had previously been in dispute as to the various constituents of this oil. Their results show its composition to be :—Glycerides of oleic acid, 45·4%; of linolic acid, 40·9%; of palmitic acid, 7·7%; of stearic acid, 3·5%; of arachidic acid, 0·4%; and of lignoceric acid, 0·2%, together with 1·7% of unsaponifiable matter.

It is, of course, well known that the rise of temperature resulting from the rapid oxidation of highly dispersed quantities of fatty acids less saturated than oleic acid or their glycerides, may bring about ignition of the mass. The observation of A. Welter[31] that the soda soaps of these acids when dry, and in flake or powder form, are equally capable of oxidation and consequently heating, is of distinct technical importance. He quotes a case in which about half a ton of dry powdered soap, prepared from cotton-seed oil, developed such a rise in temperature that in half an hour it had charred to a coke-like mass. Olive oil soaps show no tendency to such an increase in temperature. W. B. Smith,[32] who has examined the fatty acid obtained from soya bean oil, which had an iodine value of 134, states that the acids consist of linolenic acid, 2–3%; linolic acid, 55–57%; oleic acid, 26–27%; saturated fatty acids, 9–10%.

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[27] *Cotton Oil Press*, 1922, **5**, [12], 36.

[28] *Ibid.*, 1922, **5**, [9], 31.

[29] *J. Ind. Eng. Chem.*, 1921, **13**, 919; *J.*, 1922, 21A.

[30] *J. Amer. Chem. Soc.*, 1921, **43**, 2696; *J.*, 1922, 222A.

[31] *Chem. Umschau*, 1922, **29**, 151; *J.*, 1922, 508A.

SOLID FATS.

The composition of the glycerides of which oils and fats are composed is of much interest, but no satisfactory method has been suggested yet whereby they may be isolated in anything approximating to quantitative measure from the natural mixtures in which they occur. It has been known for a long time that mixed glycerides occur in the various oils and fats, and there can be no doubt that the composition and proportion of these glycerides very markedly affect such properties as the texture and melting-point of solid fats. These properties are of great importance in the manufacture of margarine and other fatty mixtures, but for the present manufacturers are dependent upon experience and the results of trial blends when adjusting the proportion of the constituents of their products. Crystallisation from solvents has been tried as a means of separation by many workers, with very limited success. J. Dekker[33] has applied this method to solutions of beef fat in ether, but results of his very extended series of crystallisations carry us no further than has been done by earlier workers. From an examination of three fractions melting respectively at 70°, 63°, and 58° C., he has presumed the presence of tristearin, distearopalmitin, and dipalmitostearin in the fat. By fractionating the methyl and ethyl esters of the fatty acids obtained from butter fat F. Frog and S. Schmidt-Nielsen[34] conclude that the percentage composition of the acids is:—Acetic, a trace; butyric, 3·4%; caproic, 3·3%; caprylic, 1·9%; capric, 3%; lauric, 3·7%; myristic, 12·9%; palmitic, 20·8%; stearic, 6·2%; oleic, 27·0%; and unidentified acids, 9·8%. They suggest, possibly with reason, that some of the unidentified acids arise from the feeding materials, although the cows yielding the milk from which the fat was obtained were fed on a standard mixed diet.

MARINE ANIMAL OILS.

The investigation carried out on behalf of the Medical Research Council by J. C. Drummond and S. S. Zilva,[35] into the methods of manufacturing cod-liver oil in Norwegian factories, and their effect upon the vitamin content of the oils, has cleared up many points which have been in dispute for a long time. Oils made by modern processes, *i.e.*, the steamed oils, which are almost always light in colour, have a vitamin value as high, if not higher, than that of the old "rotted" oils which were almost invariably of a brown shade. Indeed, it would appear that the method of preparation has less influence upon the vitamin content of the oil than changes in the diet or the physiological state of the fish at various seasons. It is particularly interesting to note that the authors have clearly established the fact that oils intended for medicinal use need not be made from cod livers, and that some other fish liver oils, notably that of the coal fish, are usually superior to cod-liver oil in their content of vitamin A. M. Tsujimoto[36, 37] has greatly extended his already wide investigations into the nature of the shark, ray, and other marine-animal liver oils. It is of interest to find that squalene is not an invariable constituent of the unsaponifiable matter of these oils, as is evidenced by the fact that kagurazame oil, obtained from the liver of *Hexanchus corinus*, consists mainly of two new dihydric alcohols having the formulæ $C_{20}H_{42}O_3$ and $C_{20}H_{40}O_3$, squalene being absent. The alcohols have been named batyl and selachyl alcohols respectively. These alcohols form the principal constituents of the unsaponifiable matter of the liver oils of a number of other species, whilst in still others they are found associated with squalene. T. Lexow,[38] who has examined the liver oil of the prickly dog-fish (*Acantheas vulgaris*), found it to contain upwards of 12% of unsaponifiable matter, in which neither squalene nor higher alcohols could be detected. The cholesterol test is responded to, but the acetate melts below 100° C. It is not impossible, as our information concerning these constituents of the unsaponifiable matter is increased, that a means of identifying at least classes of these oils may be derived from this work.

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[32] *J. Ind. Eng. Chem.*, 1922, **14**, 530; *J.*, 1922, 768A.

[33] *Pharm. Weekblad*, 1922, **59**, 305; *J.*, 1922, 333A.

[34] *Biochem. Zeits.*, 1922, **127**, 168; *J.*, 1922, 306A.

[35] *J.*, 1922, 280T.

WAXES.

Montanic acid, to which the formulæ $C_{28}H_{56}O_2$ and $C_{29}H_{58}O_2$ have variously been ascribed, has hitherto been regarded as the only acid present in montan wax. By fractionating the methyl ester of the crude acid, H. Tropsch and A. Kreutzer[39] have isolated two acids having the equivalent weights of 410·7 and 439·0, and m.ps. 82° C. and 86°–86·5° C., respectively. It is concluded that the former of these acids, for which the name carboceric acid is suggested, has the formula $C_{27}H_{54}O_2$. It is probably identical with an acid identified in Chinese wax by Gascard.[40] The acid of higher melting point, having the formula $C_{29}H_{58}O_2$, was esteemed

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[36] *Chem. Umschau*, 1922, **29**, 27, 35, 43 ; *J.*, 1922, 222A.

[37] *J. Chem. Ind. Japan*, 1922, **25**, 252 ; *J.*, 1922, 598A.

[38] *Chem. Umschau*, 1922, **29**, 59 ; *J.*, 1922, 300A.

[39] *Brennstoff-Chem.*, 1922, **3**, 49 ; *J.*, 1922, 208A.

[40] *J.*, 1920, 495A.

to be pure montanic acid. In the benzene extract of lignite another acid having the formula $C_{25}H_{50}O_2$ was also identified. G. Schicht A.-G. and A. Grün[41] claim the preparation of synthetic waxes by oxidising aliphatic hydrocarbons of high molecular weight by means of an excess of oxygen at a temperature of at least 150° C. The products of oxidation are divided into a solid and semi-solid portion by pressing, or by means of organic solvents. The solid waxes thus obtained closely resemble beeswax.

HARDENED FATS.

It is interesting to find that the opinion expressed in the Reports of last year that the highly successful application of the process of hydrogenation to fats is now acting as a deterrent to its further extension, is very emphatically supported in a statement by W. Normann,[42] who first discovered the possibility of hydrogenating glycerides in the liquid state. Normann states that the fat-hardening industry in America is in a parlous condition because the margin between the price of liquid oils and that of natural hard fats is less than the working costs of hardening. The author of this statement might well have gone farther by saying that since cottonseed oil, the oil which has been most largely employed in the hardening process in the United States, has been of the same value as lard, and for a period has even been dearer, the possibility of producing from it a hardened fat to compete with lard is obviously impossible.

The rapidity of the technical application of Normann's discovery has been phenomenal, as is made clear by the fact that only three plants were operating in 1910, and they were struggling with the various difficulties of the process, whereas after twelve years no less than about 75 factories have, by their very efficiency, restricted their own operation. Practically no developments of the process fall to be recorded during the year, but there is no doubt that, given the necessary stimulus provided by sufficient price margins in the oil and fat markets, progress will be made on the lines indicated by E. R. Bolton,[43] *i.e.*, a continuous process with a fixed catalyst capable of revivification *in situ*, delivering oil without appreciable loss of catalyst.

[41] E.P. 183,186 ; *J.*, 1922, 719A.
[42] *Z. angew. Chem.*, 1922, **35**, 437 ; *J.*, 1922, 469R.
[43] *J.*, 1922, 384R.

PAINTS, PIGMENTS, VARNISHES, AND RESINS.

By R. S. MORRELL, M.A., Ph.D., F.I.C.,

Messrs. Mander Brothers, Wolverhampton.

A REVIEW of the literature of the paint and varnish industry shows that the published communications from America and from Germany are numerous, especially from the former country. The continuous stream of contributions from the research department of the U.S. Paint Manufacturers' Association marks energetic investigation of the problems of to-day and research on fundamentals, which in due course will pave the way to the discovery of new properties, and to the production of better protective coatings. In such a number of papers it is impossible to ensure uniformity of quality, and some may show results which require careful confirmation. Nevertheless, there is energy in the work, and encouragement on the part of the producer and the user. With no organised research this country runs the risk of being left behind in an industry which was peculiarly British in its quality, reliability, and value. In almost every previous report reference has been made to the small number of English contributions, and this year the defect is very noticeable. In any report on progress, in which reference is made to German contributions, care must be taken to decide that such are not merely repetitions of work done by investigator in other countries, especially in England. It has been the experience of the writer of this report to find previously published work either unacknowledged or the results stated so that they rank as German discoveries.

In a survey of the year's work it would appear as if special attention had been paid to problems of catalysis of drying oils, to the constitution and properties of colophony, to the fineness of grinding of pigments, and to the problems of flow in paints and varnishes. The language of the school of colloid chemists is being used by investigators in the industry with a certain lack of precision which is not helpful to careful research. There is a tendency to neglect the systematic examination of the relationships between physical properties and chemical composition, and to put down changes as being due to alteration in dispersion, or even to neutralisation of electric charges. The neglect of problems of structural formulæ may be caused by lack of encouragement to workers in this field of research, and by the influence of the catalytic school of chemists, who deal generally with systems far simpler than those encountered in the paint and varnish industry. W. B. Parker[1] states that during the last twenty-five years no paper dealing with the chemical properties of resins has been contributed from British Universities or Technological Colleges, and there is only one British investigator, assisted by collaborators, who has published results recently. If real progress is to be made in the future it must be sought for in the investigation of the relationships between chemical constitution and physical properties.

DRYING OILS.

A Committee on Contact Catalysis appointed by the American National Research Council has recently issued a report, in which the facts and theories of catalysis are critically reviewed. W. D. Bancroft[2] has published a summary of the findings of the committee, and a few extracts may be of interest in considering the problems of the drying of vegetable oils. In certain cases of contact catalysis (*cf.* the action of metallic lead as a drier of linseed oil) it is presumed that definite intermediate compounds are formed. In other cases no definite intermediate compounds are formed, but adsorption occurs, producing many indefinite substances.

E. F. Armstrong and T. P. Hilditch[3] have found that in the partial hydrogenation of ethyl oleate, in addition to stearic acid isomeric oleates are formed—a fact that must not be overlooked in considering the oxidation of a drying oil. For catalysis to occur the reacting substances must be converted rapidly into active modifications, or into active compounds. The suggestion that catalytic agents emit infra-red radiations,[4] and that these radiations cause catalysis, seems, in the opinion of the Committee, to be quite inadequate to account for the phenomena. The functions of "catalytic agent" and "promoter" are stated to be that of activating either of the interacting compounds. If the given catalytic agent adsorbs or activates two substances in the wrong parts of the molecule it may easily retard instead of accelerate the reaction. Any strongly adsorbed solid,[5] liquid, or gas may act as a catalytic poison, and this should be distinguished from cases in which the catalytic agent sinters together, so as to occupy less surface and to diminish the superficial activity.

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[1] *J. Oil and Col. Chem. Assoc.*, 1922.

[2] *J. Ind. Eng. Chem.*, 1922, **14**, 326, 444, 545.

[3] *J.*, 1922, 304R.

[4] W. McC. Lewis, *J. Amer. Chem. Soc.*, 1920, **42**, 2190.

[5] E. B. Maxted, *Chem. Soc. Trans.*, 1921, **119**, 225.

K. W. Rosenmund and F. Zetzsche[6] have made successful use of "partial poisoning" to stop a reaction at any given point. It is evident that catalytic agents activate certain molecules in different ways, *e.g.*, alcohol is transformable into ethylene, and water by an alumina catalyst, or into aldehyde and hydrogen by a nickel catalyst. The application of Rideal's proposal to connect overvoltage with contact catalysis has no direct bearing on the oxidation problems of linseed oil. The idea of catalytic agent and promoter finds a parallel in the use of two driers of widely different activity, *e.g.*, lead and manganese. Certain substances, *e.g.*, pyridine, in very small quantities, greatly retard the activity of lead and manganese driers, thereby acting as poisons. The report contains the results of the examination by W. C. Bray[7] on the catalytic oxidation of carbon monoxide in air in the presence of various oxides, *e.g.*, cobalt, manganese, copper, silver, etc. The actual catalysis involves a dynamic equilibrium, in which the oxide of the metal should oxidise carbon monoxide to carbon dioxide and be restored to its original condition by the oxygen of the air at the temperature at which the change operates. The catalysts used by Bray were highly absorbent porous materials and could be poisoned by adsorbed water vapour, but if the temperature were raised to 70°–90° C. the activity was regained. The concentration of the carbon dioxide produced must be considered as exerting a retarding action. One of the most active catalysts was a mixture of 60% manganese dioxide and 40% cupric oxide, operating as low as 0° C. The great activity of the mixed catalyst compared with that of the component oxides separately is most striking, and moreover the mixed catalyst adsorbs carbon dioxide much less than manganese dioxide alone. Bancroft states that in the examination of catalytic reactions it is necessary to determine in what cases definite intermediate compounds are formed, and what these compounds are; secondly, to determine what bond and contra-valencies are opened when adsorption takes place, and to show that the opening of these bonds and contra-valancies accounts for the formation of the reaction products, presuming that a bond consists of two electrons held jointly by the two atoms in question.

Armstrong and Hilditch[8] in their criticism of the Report, state that the adsorption school of physicists and intermediate-compound group of organic chemists have developed theories which are on closely-converging lines. They suggest that the next move should be a definite acceptance of the above fact by both sides, followed by a mutual exchange of views so as to facilitate further progress.

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[6] *Ber.*, 1921, **54**, 435, 638, 1092; *J.*, 1921, 321A, 368A, 448A.
[7] *J. Ind. Eng. Chem.*, 1920, **12**, 217; 1922, **14**, 547.
[8] *J.*, 1922, 304R.

S. Coffey[9] has shown that in the oxidation of linseed oil by driers the course of oxidation is modified. The induction period is shortened, but there is a lowering of the final oxygen absorption, *e.g.*, the percentages of oxygen absorbed by linseed oil in the presence of lead monoxide, red lead, lead acetate, cobaltous oxide, and manganese borate are 17, 17, 24, 25, and 33% respectively; when no driers are present the oxygen absorption of linseed oil is 28·7%. The oxidation curves do not run parallel to the curve for linseed oil alone, and deviate considerably from the logarithmic curve suggested by Fokin. Carbon dioxide is evolved in the presence or absence of driers, but no trace of hydrogen peroxide was detected when driers were present.

P. Slansky[10] believes that the drying process of linseed oil can best be studied from a colloidal standpoint. When air is blown through linseed oil, the oil becomes more viscous, with a reduction in the iodine value, and an increase in the amount of hydroxy acids. After 15½ hrs. a very viscous oil was obtained, soluble in ether and chloroform and containing 39% of hydroxy acids. After 18 hrs. the hydroxy acids had increased by only 1%, but the oil was solid, and only partially soluble. Linoxyn owes its important characteristic of firmness to coagulation of oxidised glycerides. The coagulation point is influenced not only by the concentration of the hydroxy acids, but also by various other circumstances. Just as in the polymerisation of linseed oil by heat, so in oxidation there is also a critical coagulation point. The addition of oxygen to linseed oil is accelerated by the presence of linseed oil acids, and oleic acid promotes the gelatinisation of linseed oil, but slightly retards its setting. The importance of investigating the conditions of coagulation of the oxidised products of linseed oil is very great, as uniformity of coagulation must play a part in the production of a plane or even surface. Slansky states that linoxyn can absorb moisture up to 15% of its weight.

J. Marcusson[11] considers that fatty oils blown at the ordinary temperature, and at 120° C., undergo intramolecular polymerisation, whereas at higher temperatures (200°–300° C.) the polymerisation is bimolecular. A fish oil blown at 230° C. for 7 hrs. gave a molecular weight of 1200, against an original value of 784.

F. Fritz[12] states that linoxyn on exposure gradually becomes viscous and soluble in alcohol, with the formation of fatty acids, even when the linoxyn is kept under water, and P. Slansky[9] notes that the moisture absorbed by linoxyn exercises a saponifying action on that substance.

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[9] *Chem. Soc. Trans.*, 1922, **121**, 17; *J.*, 1922, 182A.

[10] *Z. angew. Chem.*, 1921, **34**, 533; *J.*, 1921, 904R, 817A.

[11] *Mitt. Materialprüf*, 1921, **38**, 313.

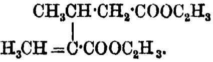
[12] *Chem. Umschau*, 1921, **28**, 29.

F. H. Rhodes and K. S. Chew[13] have investigated the action of vanadium compounds as driers. Vanadium pentoxide heated at 350° C. with linseed oil for $2\frac{1}{2}$ hrs. or ammonium metavanadate heated with linseed oil at 300° C., or resins heated at 250° C., with the two vanadium compounds mentioned were compared with lead, manganese, and cobalt driers in 1% solution in oil. Vanadium drying oil is more active than the corresponding manganese and lead oil, but it is inferior to a cobalt oil. Vanadium oils are darker in colour and give a brown skin.

L. L. Steele and G. G. Sward[14] find that the acidity of oils is best determined by using as solvent equal parts of alcohol and benzine during the alkalimetric titration.

The paper by K. H. Bauer and K. Herberts[15] on tung oil has been criticised by R. S. Morrell,[16] who points out that the transformation of the methyl ester of α-elæostearic acid into β-elæostearic methyl ester can be brought about by distillation *in vacuo*, and the transformation of the α-acid into β-acid is not caused by saponification with alkali.

The theory of polymerisation is discussed by A. H. Salway and R. S. Morrell.[17] H. Staudinger[18] subdivides polymers into two classes: (*a*) true ploymers which contain the atomic constituents united in the same manner as in the original substances, and (*b*) false or condensed polymers produced by the interaction of two or more molecules with a rearrangement of atomic linkages, *e.g.*, dicrotonic ester from crotonic ester:



$$\begin{array}{l} \qquad\quad CH_3CH\cdot CH_2\cdot COOC_2H_3 \\ \qquad\qquad\quad | \\ CH_3CH=C\cdot COOC_2H_3. \end{array}$$

Salway considers that in the polymerisation of oils the fatty acid radicles of a fat are partially dissociated from the glyceryl radicle, and in this condition are capable of reacting chemically with the unsaturated linkages of a second fatty acid radicle, thus producing a partial saturation of the fat. The theory would account satisfactorily for many of the observed facts in polymerising fatty oils. Morrell criticises the views of Salway and brings forward certain facts concerning the polymerisation of China wood oil, which appear to support Salway's theory. The polymerisation of tung oil seems to be connected with the presence of the glyceryl radicle, by comparison with the properties of the methyl ester of an elæostearic acid.

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[13] *J. Ind. Eng. Chem.*, 1922, **14**; *J.*, 1922, 334A.

[14] *Ibid.*, 1922, **14**, 57; *J.*, 1922, 260A.

[15] *Chem. Umschau*, 1922, **29**, 229.

[16] *J.*, 1918, 181T; 1922, 328T.

[17] *J. Oil and Col. Chem. Assoc.*, 1922, **5**, 16, 22.

[18] *Ber.*, 1920, **53**, 1073.

The paper by J. Marcusson[19] on the polymerisation of oils is essentially a repetition of work which has already been published, and has been quoted in previous Annual Reports.

The paper on the relationship between the refractive indices and the chemical characteristics of oils and fats by G. F. Pickering and G. E. Cowlishaw[20] is of interest to readers of this section, in so far as the results concern oxidised drying oils. If the refractive index were affected so as to establish a relationship to the degree of oxidation the results would be valuable. The complete equation :—

$$N_d = 1{\cdot}4643 - 0{\cdot}000066(\text{S.V.}) - 0{\cdot}0096(\text{A.V./S.V.}) + 0{\cdot}000171(\text{I.V.})$$

does not apply to tung oil, to which no reference is made in the paper. The investigation of changes in refractive index of China wood oil during oxidation as well as the changes occurring during thickening would be valuable. The process of drying is so complex that definite connexion between refractives indices at different stages must be difficult.

In the investigation of special drying oils the results published during the year include a confirmation by M. Tsujimoto[21] of the formula $C_{22}H_{34}O_2$ for clupanodonic acid. Clupanodonic acid was obtained from Japanese sardine oil, in which it is present to the extent of 20%. Tsujimoto considers that it is a probable component of sea- and fresh-water fish oils. Perilla oil has been shown by Bauer[22] to consist of a mixture of palmitic and linolic acids, and several geometrically isomeric linolic acids.

A. H. Sabin[23] states that perilla oil has secured a permanent place in the varnish industry in America, so much so that all offerings of the oil are taken usually at a price above that of linseed oil. It contains 12% of saturated acids. The examination by H. A. Gardner and A. Reilly[24] of Japanese tung oil from *Aleurites cordata,* from the Fukui Province, has shown that it may be used to a considerable extent for the same purposes as Chinese tung oil. The iodine value (150·2) and index of refraction (1·4981) are lower than those of the Chinese variety. The seed contains 51% of oil. Under the A.S.T.M. standardised heat test the oil yields a viscous liquid and does not gel. When the oil is heated between 250° C. and 315° C. for several hours it dried in 43 hrs. to a clear film, and it is the only one of the series which gives a clear film without driers ; moreover the time of drying compared favourably with that of heavy bodied linseed oil (58 hrs.).

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[19] *Z. angew. Chem.*, 1922, **35**, 543 ; *J.*, 1922, 867A.

[20] *J.*, 1922, 74T.

[21] *Chem. Umschau*, 1922, **29**, 261 ; *J.*, 1922, 719A.

[22] *Farben-Zeit.*, 1922, **27**, 2756 ; *J.*, 1922, 719A.

[23] *J. Ind. Eng. Chem.*, 1922, **14**, 775.

[24] *Circ.* 138, 1921, *Paint Manuf. Assoc., U.S.A.* ; *J.*, 1922, 904A.

Lumbang (candle nut) oil from *Aleurites moluccana* has been shown by A. P. West and Z. Montos,[25] to remain fluid up to 315° C., and if held at that temperature it begins to distil regularly, gelatinising when one-third has been volatilised. Although extracted from *Aleurites* it does not contain elæostearine, but glycerides of linolenic (6·5%), linolic (33·4%), and oleic acid (56·9%), and solid acids (2·8%).

H. A. Gardner and E. Bielouss[26] indicate a method for transforming less unsaturated substances, *e.g.*, petroleum and semi-drying oils, into substances which may have a useful drying value. When mineral oils containing $C_{17}H_{35}$ and $C_{26}H_{34}$ were chlorinated to add three or four chlorine atoms, and the products dechlorinated to remove HCl, products with iodine values of 70–130 were obtained. Soya-bean and cotton-seed oils, when subjected to similar treatment, gave substances of increased drying properties.

In a review on the composition of soya bean oil by Matthes and Dahle,[27] the presence of palmitic acid, and not stearic acid, together with 2% of linolenic, 55% linolic, and 26–27% oleic acid, is of interest. E. A. Tschudy[28] points out that in the determination of linseed oil in mixtures by means of the iodine and hexabromide values of the fatty acids the error may vary from 17 to 18% of the linseed oil present, which is not a satisfactory outlook for the estimation of adulteration of linseed oil.

RESINS.

The importance of investigations on the constitution of abietic acid cannot be overestimated. The concensus of opinion is in favour of the formula $C_{20}H_{30}O_2$, but the representation of its numerous isomers is very controversial. Recent literature on the subject is considerable and progress can be reported. Seidel[29] identified three abietic acids with melting points that depend to some extent on the history of the sample, because the amorphous forms have lower melting points than in the crystalline state, and the amorphous varieties change slowly into the crystalline form on heating for periods peculiar to the isomeric forms. The boiling points of the three modifications in an absolute vacuum (green cathode light) of the α-acid, β-acid and γ-acid are nearly constant, especially the β- and γ-acids. Seidel is of the opinion that the theory of the acids in ordinary rosin being anhydrides, whereas the crystalline acids are hydrates, is incorrect.

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[25] *Philippine J. Sci.*, 1921, **18**, 619.

[26] *J. Ind. Eng. Chem.*, 1922, **14**, 619; *J.*, 1922, 639A.

[27] *Oil and Col. Tr. J.*, 1922, 221.

[28] *J. Ind. Eng. Chem.*, 1921, **13**, 941; *J.*, 1922, 21A.

[29] *Dissertation, Mannheim,* 1913.

L. L. Steele,[30] accepting the view that rosin contains abietic anhydride and using Knecht and Hibbert's method of hydration by 98% acetic acid, obtained from W. W. American rosin a 50% yield of an acid with a constant melting point 161°–165° C. The acid could be recrystallised from alcohol, or from glacial acetic acid. The acid value was 186, the iodine value (Wijs, ½ hr.) 168·5–171 (calculated for two double bonds, 167·9) and a_D=80° (Schulz obtained –77·9°). These melting points do not agree with the figures given for either α-, β-, or γ-abietic acid. The remainder of Steele's paper is concerned with the preparation and examination of a number of precipitated metallic abietates, lead, manganese, cobalt, and nickel; their metallic contents are all slightly low, due to the presence of traces of occluded sodium abietate, but all are soluble in benzene. Iron and chromium abietates are of indefinite composition.

For recent details as to the preparation of metallic resinates reference may be made to an article by M. de Keghel.[31]

L. Ruzicka and J. Meyer[32] by the distillation of American colophony at 1 mm. pressure, obtained an acid of b.p. 200°–210° C., with a melting point, 158° C., which agrees with the melting point of α-, β-, or γ-acids which had been previously strongly heated. The reduction of this acid gave a mixture of dihydro and a tetrahydro acid.

A. J. Virtanen[33] has prepared a series of hydrogenised retenes, and after comparing them with the hydrocarbons of rosin oil, concluded that all resin acids contained a hydrogenised retene nucleus. There is now practical unanimity upon that conclusion, but there is still disagreement as to the position of the side groups.

Soane[34] in a careful summary of the literature on rosin and rosin oil, states that, in the meantime, it is safe to assume that the differences in the relative position of the methyl and isopropyl side-chains may account for the isomerism of the resin acids. Rosin oil consists essentially of a mixture of hydrocarbons of the hydrogenised retene type, together with such decomposition products, approaching a benzenoid character, as result from a cracking process, as the higher temperatures of distillation are reached.

A. Grün[35] suggested that abietic acid results from a combination of α-pinene and β-pinene with subsequent oxidation of a methyl group to a carboxyl group, and that the various rosin acids are accounted for by different modes of combination. The following formulæ, taken from Soane's paper, will indicate the suggested constitutional formulæ, as well as the connexion with retene and phenanthrene. It is evident that they are modifications of the constitutional formula of abietic acid, proposed by T. H. Easterfield and Bagley in 1904.

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[30] *J. Amer. Chem. Soc.*, 1922, **44**, 1333; *J.*, 1922, 558A.

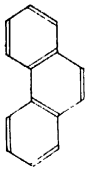
[31] *Chem. Trade J.*, 1922, 289.

[32] *Helv. Chim. Acta*, 1922, **5**, 315; *J.*, 1922, 482A.

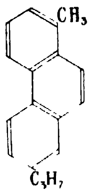
[33] *J. Oil and Col. Chem. Assoc.*, 1922.

[34] *Annalen*, 1921, **424**, 150.

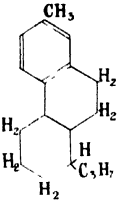
[35] *Z. Deuts. Oel- u. Fett-Ind.*, 1921, **41**, 49; *J.*, 1921, 311A.



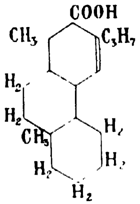
Phenanthrene $C_{14}H_{10}$.



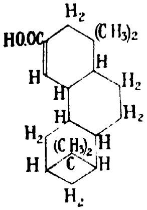
Retene, $C_{18}H_{18}$.



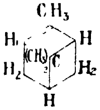
Hydrocarbon $C_{18}H_{24}$ from rosin oil (Schultz).



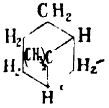
Abietic acid $C_{20}H_{30}O_2$ (Easterfield and Bagley, 1904, with CH_2 added).



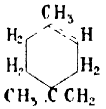
Abietic acid (Grun, 1921).



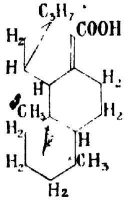
α-Pinene $C_{10}H_{16}$.



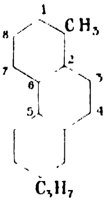
β-Pinene



Dipentene $C_{10}H_{16}$.



Pinabietic acid $C_{20}H_{30}O_2$ (Virtanen).



Retene.†

† According to Ruzicka, the remaining CH_3 group and the COOH group in retene may occupy one of the following positions :— CH_3:COOH = 6.3, 5:4, 6:1, 2.8, 2:7.

K. G. Jonas[36] criticises the constitutional formulæ of abietic acid on a phenanthrene and retene basis. He has prepared hexahydrogenated phenanthrenes and retenes and compared their physical constants with those of hydrocarbons obtained from abietic acid and concludes that they do not belong to the same series.[33]

Abietic acid obtained from the fresh oleoresin of *Pinus sylvestris* gave two liquid esters, separable by fractional distillation, and which, by rapid saponification, yielded two different α-abietic acids, whilst β- and γ-abietic acids furnished simple tricyclic esters. By the esterification of α-abietic acid by hydrochloric acid and methyl alcohol another ester was obtained different from the two mentioned above, which on saponification gave another α-abietic acid, which he states is an unsaturated tetracyclic *a*-abietic acid. He criticises the conclusion drawn by Wienhaus [37] that rosin acids on treatment with mineral acids pass into a more unsaturated form (sylvic acid form). Jonas considers that Virtanen's formula for pinabietic acid is improbable and favours the formula of Grün as to abietic acids being condensation products of terpenes. From the oleoresins of *Pinus sylvestris* he obtained pinene and abietic acids, also hydrocarbons $C_{20}H_{30}$ and $C_{20}H_{32}$, *i.e.*, diterpenes, together with an alcohol $C_{20}H_{32}O$, and an aldehyde $C_{20}H_{30}O$, intermediate products of the resin acids, which could be formed from terpenes. Unfortunately, no mention is made by him of the work of Ruzicka and Seidel, whose results would appear to be reliable. The difficulty in deciding between the proposed constitutional formulæ lies in the fact that the oleoresins themselves differ probably in composition, depending on the source of origin, as in the case of varieties of turpentine; moreover, the conditions of preparation of rosin vary greatly as to temperature conditions, so that one may expect similar differences to those occurring in the formulæ for the terpene hydrocarbons. Undoubtedly the formulæ on the retene basis are as correct as those on the terpenoid basis, and the bewildering number of isomers may be partly explained on the basis of Ruzicka's representation and on polymorphic forms.

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[36] *Chem. Umschau*, 1922, **29**, 223.

O. Aschan [38] has separated from the liquor of sulphate cellulose factories, as well as from American and Finnish colophony, a new series of resin acids, which he provisionally terms colophenic acids. These have the general formula $C_nH_{2n-10}O_4$ and are monobasic, being pale yellow in colour. The alkali salts are dark yellow or brownish yellow, and soluble in cold water, distinguishing them from the salts of other resin acids. These acids are: hexadecacolophenic acid $C_{16}H_{22}O_4$, m.p. 96°–105° C., heptadecacolophenic acid, m.p. 100°–105° C., octodecacolophenic acid, m.p. 90°–100° C. The colophenic acid of Aschan is regarded by W. Fahrion [39] as identical with oxyabietic acid, which he had discovered to be formed by the autoxidation of colophony, but to this view Aschan demurs, being of opinion that the product examined by Fahrion, and described as oxyabietic acid, could not be a pure substance. Aschan [40] states that colophenic is an excellent material as a varnish resin, its solutions in ethyl and methyl alcohol giving a film which becomes very hard on exposure to air. Levy's abietene and Virtanen's pinabietene [41] must be regarded as structurally identical

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[37] *Dissertation, Heidelberg*, 1913.
[38] *Ber.*, 1921, **54**, 867; *J.*, 1921, 439A.
[39] *Ibid.*, 1922, **55**, 700; *J.*, 1922, 300A; 1921, 780A.
[40] *Ibid.*, 1922, **55**, 1, 3; *J.*, 1922, 183A.
[41] *Cf. J.*, 1921, 594A.

7.13-dimethyl-2-isopropyl-5.6.7.8.9.10.13.14-octahydrophenanthrenes.[42] E. Stock[43] is also of the opinion that colophony is not an anhydride and confirms the results of Tschirch on the production of α-, β-, and γ-acids from abietic acid. Moreover, he confirms the tendency of heat to transform abietic acid from a colloid to a crystallised condition. Recrystallised abietic acid might contain isomers, but they cannot be detected by melting points or boiling points *in vacuo*. In addition to the various forms of abietic acid American rosin contains 10% of resene, 0·5% of ethereal oils, and 0·5% of impurities.

The commercial applications of colophony are described by an anonymous author.[44] The yield of oleoresin from the stock pine is better than from the long-leafed pine.[45] The esterification of fossil resins and the production of neutral varnishes from them is discussed by H. A. Gardner and P. C. Holdt.[46]

A review of the question of purchasing specifications for resins and shellac is given by W. B. Parker.[47] The author points out that with the exception of shellac and rosin no serious attempt has been made to develop the existing knowledge of these important raw materials into standards which could be made the basis for their purchase. The advent of the so-called synthetic resins must ultimately force those who deal in natural resinous products to recognise that unless they keep pace with the modern demand for exactitude in raw materials their businesses must perish. The author admits that difficulties must be overcome before the specifications put forward by him become generally acceptable, but he believes that they could be surmounted by determined and concerted action. For practical purposes he considers the following factors suitable for specification purposes: (1) Chemical: moisture, %; mineral matters, %; total non-resinous matters, %; iodine value; acid value; saponification value (hot); rational composition, % (partial or complete); (2) Physical: Gross solubility, % in specific solvents, colour, size, cleanliness, habit (when of positive value). The author has considered some actual values for a few of the most utilised resinous materials and has put those values into draft specifications with the object of showing how they could be utilised in compiling specifications. In drafting the specifications Parker has depended almost entirely upon the test data obtained in the chemical department of the British Thomson-Houston Co. He is of opinion that the work ought to be continued by a committee of the Oil and Colour Chemists' Association. The standards laid down by Parker are almost too high to meet with general approval, although the importance of investigating the fundamental properties of the raw materials ought to be recognised. It is work to be done by a Research Association or a Paint and Varnish Institute.

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[42] *Ber.*, 1922, **55**, 2944; *J.*, 1922, 947A.

[43] *Farben-Zeit.*, 1921, **27**, 156, 221, 287, 353, 416.

[44] *Chem. Trade J.*, 1922, 567.

[45] A. Carey, U.S.A. Forest Service; *O.C.Tr. J.*, 1922, 1935.

[46] *Circ.* 151, *Paint Manfrs. Assoc. U.S.*; *J.*, 1922, 947A.

[47] *J. Oil and Col. Chem. Assoc.*, 1922.

R. R. Majima[48] has made another valuable contribution on the chemistry of Japan lac. Hydrourushiol is present to the amount of 10% in urushiol (the main component of Japan lac). In addition, the following substances are probably present: $C_6H_3(OH)_2.(CH_2)_7CH : CH(CH_2)_5CH_3$, which, on oxidation, gives heptanal and the acid $C_6H_3(OH)_2.(CH_2)_7COOH$, or its homologues, and $C_6H_3(OH)_2(CH_2)_7CH : CH.(CH_2)_4CH : CH_2$, which is oxidised to formic acid, and the same aromatic substances as the preceding compound. Analysis of the bromide and ozonide of its dimethyl ether and the volume of hydrogen absorbed during reduction indicate that it contains two double bonds in the molecule. Urushiol is a mixture of compounds which differ from one another in the number and position of the double bonds in the long normal carbon chain; in this respect they resemble the vegetable drying oils. So far it has been impossible to separate urushiol into its components. Nevertheless all are converted by reduction into the same hydrourushiol, and urushiol has a mean molecular formula $C_{21}H_{32}O_2$ or $C_6H_3(OH)_2C_{15}H_{27}$. Burmese lac (*Melanorrhœa usitata*), "thitsi," contains thitsiol, a homologue of isohydrourushiol, and as judged by the amount of hydrothitsiol produced on reduction it cannot amount to more than one-third of the original material, whereas Japanese or Chinese lacquer gives hydrourushiol, or hydrolaccol to the extent of 90%. Indo-Chinese lac, probably from *Rhus succedanea*, contains laccol, which is easily reduced to hydrolaccol $C_{23}H_{40}O_2$ (isomeric with hydrothitsiol), and is a higher homologue of hydrourushiol. Formosa lac (*Seneocarpus vernicifera* and *Rhus orientalis*) contains laccol as main constituent. The toxic action of Japan lac is due to urushiol. Laccol and thitsiol are equally poisonous, but less than urushiol.

Tschirch[49] ascribed to aleuritic acid obtained from lac the formula of a dihydroxytridecylic acid. C. Harries and W. Nagel[50] have examined aleuritic acid prepared from shellac by treatment with *N*/5 caustic potash, whereby the potassium salt was separated. A 30% yield of an acid, m.p. 100° C., was obtained. On reduction with hydriodic acid palmitic acid was obtained, so that aleuritic acid appears to be trihydroxypalmitic acid $C_{16}H_{19}O_2(OH)_3$. A report[51] on lac, turpentine, and rosin has been presented by a special committee appointed by the Imperial Institute Committee for India to consider the possibility of increasing the trade in Indian gums, resins, and essential oils with the other parts of the Empire. Although India contributes 94% of the world's annual production of lac, the industry is not well organised, and adulteration of the lac products is common. Recommendations are made for improving the efficiency of the industry, and in the main confirm the findings of the Report on Lac and Shellac, by Lindsay and Harlow.[52] Special interest attaches to the possibility of obtaining supplies of turpentine and rosin from India, which is the only part of the British Empire that produces these raw materials in quantity. It is estimated that the present production of 50,077 cwt. of rosin and 152,442 galls. of turpentine in 1920, should in the future reach 440,000 cwt. and 1,600,000 galls. respectively. The Committee consider that every effort should be made to increase production and to provide adequate transport facilities in the forests.

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[48] *Ber.*, 1922, **55**, 172, 191; *J.*, 1922, 182A.

[49] *Die Harze u. Harzbehälter*, II., 257.

[50] *Chem. Umschau*, 1922, **18**, 135; *J.*, 1922, 474A.

[51] *Report, Indian Trade Enquiry Imp. Inst.*, 1922; *J.*, 1922, 203B.

The solubility of shellac in alkalis and alkaline salts has been examined by H. Wolff,[53] who considers that the solution process is of the nature of peptisation.[54]

The loss of alcohol-solubility of bleached shellac is said to be due to the coagulating effect of hydrogen ions arising from the precipitation of the lac by acids and the maintenance of solubility by storage under water is due to the diminution of the acid concentration.

From a comparison of ten artificial resins with natural shellac E. Fonrobert[55] concluded that they were inferior in hardness and elasticity with the exception of Resinol M. and Albertol, but superior in lustre and polish to the natural shellac. He considers that the slow volatilisation of the phenols may be the cause and hints at a danger if the artificial resinous material remain in contact with the human skin for any length of time. A. Bülteman[56] maintains the great superiority of the varieties of Bakelite in insulating properties over the natural resin. Attempts have been made to connect peculiarities in constitutional formulæ with the power of a compound to assume a resinous condition. W. Herzog and J. Kreidl[57] indicate that the group CH·CH·CO is resinophoric, as instanced by the transformation of dibenzylideneacetone at 180° C. into a polymeric resinous compound, m.p. 85°–98° C., soluble in turpentine, benzene, and ether. Herzog[58] is of the *opinion that* $N = C = N$ *is a resinophore group as instanced* by certain ureas which yield resinous substances. He has found that thioureas can be desulphurised by heating them above their melting points so as to eliminate hydrogen sulphide-yielding polymerised carbodiarylimides. Similarly N = P = N is a resinophore group. The great difficulty about the artificial resins is their permanence as solid colloid substances and a tendency to pass slowly into a crystalloid condition, so that their value can only be decided upon after a prolonged exposure to the action of the air.

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[52] *Indian Forest Records*, 1921 ; *J.*, 1921R.

[53] *Farben-Zeit.*, 1922, **27**, 3130 ; *J.*, 1922, 771A.

[54] A. P. Laurie and Clark Ranken, *J.*, 1917, 1242.

[55] *Chem.-Zeit.*, 1922, **68**, 513.

[56] *Kunststaffe*, 1922, **66**, 76, 82.

[57] Z. *angew. Chem.*, 1922, **35**, 465, 641 ; *J.*, 1922, 771A, 988A.

[58] *J.*, 1921, 478A.

The number of patents for the preparation of artificial resin continues to increase. The majority are modifications of the formaldehyde condensation with aromatic substances in great variety. Aromatic hydroxycarboxylic acids have been condensed with formaldehyde and suitable catalysts to give resins soluble in alcohol and acetone, applicable for leather-finishing and for treating felts in the manufacture of hats.[59] Some are soluble in weak alkalis and can be used as substitutes for shellac. Hydrocarbons, *e.g.*, benzene, toluene, xylene, phenanthrene, and naphthalene, can be condensed with formaldehyde in the presence of sulphuric acid (sp. gr. 1·84) to give resins, of which those melting below 100° C. are of value for varnish-making[60]; they are soluble in acetone or benzene, but, apparently, not in alcohol. A. Koch[61] finds that harder resins can be obtained when the condensation of a phenol with an aldehyde is carried out in the presence of hydrogen and a nickel catalyst. If phenols be condensed with unsaturated hydrocarbons, *e.g.*, cresol with styrene or pinene, further condensation with formaldehyde produces resins soluble in benzene and in linseed oil, but insoluble in alkalis and alkali carbonates.[62]

PAINTS AND PIGMENTS.

A. Forster and J. Reilly[63] describe the Plauson mill, which claims to produce ultra-microscopic suspensions of particles of a wide range of substances of less than 1μ diameter showing characteristic Brownian movement. Two types of mill are described: one is a disc mill in which is applied an adjustable pressure on the suspension passing through the disc, a continuous circulation of the milled suspension, and a rapid counter-revolution of the discs at 2000 r.p.m.; the other mill consists in principle of a dismembrator in which Plauson's innovations are: (1) the rotating arm-wheel is placed eccentrically towards the base of the containing case, so that the material continually falls into the field of action instead of circulating centrifugally outside the arm-wheel range, (2) the reduction of baffles to a minimum number (two for balance), in order to obtain a maximum force of each. In the ordinary dismembrator the force is divided over a number of baffles.

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[59] G.P. 339,495; *J.*, 1922, 639A.
[60] G.P. 349,741; *J.*, 1922, 639A.
[61] G.P. 354,697; *J.*, 1922, 772A.
[62] G.P. 340,989; *J.*, 1922, 23A.
[63] *J.*, 1922, 435R.

The third innovation of Plauson is the application of extremely high speeds of revolution. The standard size of the mill is 15 litres capacity and the rotation is 3000 r.p.m. In almost every colloidal preparation the mechanical action of the mill is assisted by the addition of dispersators or accelerators acting as protective colloids. The material must be subjected to a preliminary grinding, then made into a suspension in a medium, the accelerator added and the whole run into the mill. In some cases it is not economical to aim at complete disintegration of material in one set of millings, but to allow the non-colloid material to settle out for further milling in the succeeding batch. The exact figures of power consumption are not stated, but 1000 kg. of ground raw calcium phosphate was transformed in three 15-litre machines at 9000 r.p.m. in one hour to give 85% of particles of 1μ diameter.

The chief advantage of the mill appears to be great saving of time in the grinding, even if the overhead charges be high. It is a matter of conjecture as to whether a suitable cone-mill travelling at a high rate of speed will not produce similar results. The action of the accelerator is strictly specific, and its purpose in allowing or accelerating the disintegration of particles, so as to absorb soluble electrolytes and to reduce the power consumed by the mill, requires careful adjustment.

In Traun's[64] patents for the manufacture of dispersoids the material is circulated with the required dispersing medium through a disintegrator which is run at a high speed (1000–2000 r.p.m.), and in which the grinding pressure is concentrated at a few points. The quantity of dispersing medium must be large compared with that of the phase to be dispersed, and a dispersion accelerator (a substance in which the phase to be dispersed is slightly soluble) is employed. The disintegrating machines are constructed so that the material to be dispersed is subjected to heavy localised pressure in the dispersing medium by a special rapidly rotating wheel or cylinders.[65] The general scheme would seem to differ very little from the proposals of Plauson.

A number of papers on the fineness of pigments have appeared during the year. H. A. Gardner, H. Parks, and N. Pihlblad[66] record the fineness of a pigment as a residue on a 325-mesh screen of 3-in. diameter, using Holley's method, after drying and weighing the residue. Vogt[67] uses a turbidimetric method in which the suspension of the pigment is placed above a source of light so that the rays are cut off. The obscuring power is assumed to be the total projected area of the suspended particles. Assuming spherical particles, it is shown that the obscuring power varies inversely as the diameter of the particles.

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[64] E.P. 155,836, 176,002, 176,003; *J.*, 1922, 357A.

[65] *J.*, 1921, 799A.

[66] *Paint Manuf. Assoc. U.S. Circ.*, 143, 1922; *J.*, 1922, 946A.

[67] *India Rubber World.* 1922. **66**. 347.

A. D. Luttringer[68] gives a resumé of the methods recently developed for determining dimensions of individual particles of pigments.

C. D. Holley[69] concludes, after many tests, that a 350-mesh screen gives definite information on the ease of grinding of paint pigments.

T. M. Lowry and H. McHatton[70] point out that sieves with 350 meshes to the linear inch are very troublesome to use and sieving no longer affords a practical grading. They describe an elutriator which is based on Boswell's apparatus, wherein the residue is allowed to settle in a capillary tube and the height of the column of gritty material is measured in millimetres for the indication of the proportion of coarse material in the ground sample. It is easy for a foreman with no chemical knowledge to determine by means of this instrument the quality of the powder which is being produced from hour to hour. Experiments were made to determine the diameter of particles of barytes and of quartz, which are just lifted by a vertical flow of water at stated velocities. Under identical conditions the diameters are 1·42 times as great for quartz as for barytes, the sectional areas of the particles being therefore in the ratio 2 : 1, which is practically identical with that of the gravitational forces on the particles. The lifting power of the water is therefore proportional to the area of the particle. In the discussion following the papers read by Lowry and Boswell at a joint meeting of the Faraday Society and the Oil and Colour Chemists' Association, C. A. Klein[71] criticised the specifications in which a limit is put on the residue left after screening through sieves of stated mesh. The variations in the composition of the powders as to size complying with the specification is so great as to render the specification valueless. He preferred an elutriator of the Schöne type,[72] using a number of them of varying diameters arranged in series, as by such means clearer separations are obtained. In the course of an examination by elutriator and microscope of a large number of pigments prepared by chemical or mechanical means, the range of size in the first case was invariably found to be much smaller, as also was the mean size of the particles.

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[68] *Caoutchouc and Gutta Percha*, 1922, **19**, 11308.

[69] *Paint, Oil, and Drug Review*, 1921, **72**, 16.

[70] *J. Oil and Col. Chem. Assoc.*, 1922, **5**, 82.

[71] *Ibid.*, 122.

[72] *J. Oil and Col. Chem. Assoc.*, 1920, **3**, 177.

Where pigments contain barytes or have been prepared by grinding, the range of sizes was very considerable, often varying as much as 200%, although the percentage of large particles was small.

H. Baker[73] has shown that the velocity at the centre of the elutriator is twice the apparent velocity. Klein considers that close separation of powders containing particles of many sizes can only be effected by repeated treatment of the fractions obtained by preliminary elutriation. As separating medium methylated spirit was used in place of water. He emphasised the pressing need for an agreement as to a rational and clear method of expressing the results obtained. A specification should contain the maximum diameter of the particles, and the limiting diameter of the average of the particles. In view of the increasing use of air flotation on the large scale for the separation of particles of varying sizes, the need for an accurate method of separation and determination of size of particles is obvious

A joint committee of the Association of British Chemical Manufacturers and the British Chemical Plant Manufacturers' Association[74] is drawing up standards for filter presses. The final proposals for standardisation of cast iron filter presses will shortly be presented to the General Committee, and on acceptance will be sent forward to the British Engineering Standards Association. The particulars of the original proposals were published in 1921[75] and the sub-committee has completed the revision of the proposals, and has added specifications for a standard 48-inch plate.

According to Klein[76] two interesting additions have been made to the somewhat limited number of white substances which can be satisfactorily used as white pigments, *viz.*, titanium oxide and antimony oxide. The titanium oxide pigments, which have been described by N. Heaton[77] in a lecture before the Royal Society of Arts, are in practice mixed with barium sulphate, and titanium white (the composite product) is marked in two grades, "extra" and "standard," the latter consisting approximately of 25% of titanium oxide and 75% of barium sulphate. The durability tests have shown that there is no tendency to crack or peel on long exposure, and the most durable combination has been found to be a mixture of titanium white with a proportion of zinc oxide. Titanium oxide alone has a tendency to "chalk." Titanium white is non-toxic and is unaffected by any of the destructive agencies, *e.g.*, sulphuric acid and hydrogen sulphide, to which a paint is likely to be exposed. The titanium white oxide possesses greater opacity and greater spreading power than any other white pigment.

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[73] *Geological Mag.*, 1920, **57**, 321.

[74] *J.*, 1922, 210R.

[75] *J.*, 1921, 401R.

[76] *J.*, 1922, 209R.

[77] *J. Roy. Soc. Arts*, 1922, **70**, 552 ; *J.*, 1922, 216R.

Antimony oxide (Timonox, Antox), produced by condensation of the vapour of antimony oxide obtained by roasting antimony sulphide, has been referred to in former Annual Reports. The manufacture by the Antox Syndicate, of Sydney, N.S.W., from ore of the Costerfield Mine (one of the largest antimony mines in the world) provides, by variation of the temperature at which the plant is worked, a product of colour from pure white to dull orange. Interest in these pigments has been stimulated by the controversy on the use of white lead, which culminated at the International Labour Conference held at Geneva last year. Although the new pigments, which are stated to be non-toxic, appear to have proved suitable in certain directions, it cannot be said that sufficient experience has been gained to warrant the assumption that either is capable of being used as a complete alternative for white lead or zinc oxide.

Both new pigments are stated to give the best results when mixed with zinc oxide. Titanium and antimony whites have been brought forward at a most opportune moment, and even if the ultimate demand for them does not come up to expectation they can be assured of a permanent position in the list of standard white pigments, provided they can compete economically with other pigments in use.[78]

Much has been written of the dangers of lead poisoning. Last year the Labour Conference of the League of Nations at Geneva decided for the prohibition of lead paint for the interiors of buildings, but the resolutions do not come into force until 1927. A Home Office Committee on the use of white lead in paints is still sitting, but in the meantime the Home Office, in conference with the Painters' and Decorators' Industrial Joint Council of Great Britain, has already drafted regulations for the use of white lead or lead sulphate in paints in order to give effect to the resolutions of the Geneva Convention. In the twelve regulations issued lead paint means any paint, filling, or painters' material, containing more than 2% of lead expressed in terms of metallic lead. White lead, lead sulphate, or products containing these pigments shall not be used in painting operations except in the form of paint or paste ready for use and shall not be applied by spray for interior work, nor rubbed down by a dry process. Precautions are to be taken with regard to washing and care of clothing. In these regulations the use of white lead is not prohibited for the interiors of buildings, and it remains to be seen whether in the next five years there will be a reduction in the number of certified poisonous cases, so that the prohibiting clause may be found to be too drastic. All are agreed on the great dangers of the dry rubbing-down of paints, and the success of wet rubbing-down with special waterproof sandpaper was demonstrated at the Conference of the National Federation of Master Painters and Decorators this year.

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[78] V. M. Goldschmidt, U.S.P. 1,398,191; H. H. Buckman, U.S.P. 1,411,839; *J.*, 1922, 381A; U.S.P. 1,396,924; *J.*, 1922, 22A; U.S.P. 1,402,256; *J.*, 1922, 149A.

Many maintain that the dust caused by the dry rubbing-down is the source of the trouble. The controversy respecting white lead has stimulated investigation of the properties of many other pigments with results which have benefited the industry. The replacement of white lead by other white pigments for indoor work is generally accepted, but for exteriors white-lead paint or red-lead especially for undercoats holds its own unless the pigment be in the form of an enamel, which requires a special scheme of application. A comparison of the water absorption of a white-lead paint against a zinc-white shows the superior impermeability of the former.

In 1870 Holman Hunt exposed a large number of artists' colours on canvas. Inspection of these colours by A. P. Laurie[79] shows that the present selected list of artists' pigments is reliable, with the possible exception of pale cadmium yellow and cobalt yellow. The present practice of protection by an easily removable mastic varnish is justified, and the excessive darkening of the oil on canvas is probably due to the lead driers, which are excluded from the oils and varnishes used in modern practice.

The systems of colour classification due to W. Ostwald, Hearing, and others are briefly discussed by H. Trillich,[80] who proposes a decimal system of specification wherein red, yellow, light blue, and violet are chosen as primaries. The system can be diagrammatically represented as a colour star, in which the primary colours are disposed at angular distances of 90° on the circumferences of a circle. A research[81] on colour standardisation has been undertaken by the National Physical Laboratory. The work will involve the measurement of a representative number of colours on various types of colorimeters, both scientific and commercial, and a co-ordination of the results of the various systems with a view to ascertain the most suitable basis for the standardisation and specification of colour, having regard to the requirements both of scientific accuracy and applicability to industrial processes.

By those concerned in the protection of metals by varnishes and paints the report of the Corrosion Committee of the Institute of

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[79] *J. Roy. Soc. Arts*, 1922, **70**, 432.
[80] *Farben-Zeit.*, 1921, **27**, 672; *J.*, 1922, 23A.
[81] *Report Nat Phys. Lab.*, 1921 (*Optic. Division*).

Metals[82] should be carefully studied. Two types of corrosion are recognised: (1) the general type characteristic of acid corrosion, (2) a local type characteristic of corrosion in water and salt solutions generally with the formation of an adherent scale on the metal, and the scale may contain colloid material. A theory has been developed regarding the part played by colloids in corrosion. It is pointed out in the report that an aluminium surface may be cleaned by soda to which small quantities of sodium silicate have been added without action on the metal.

Several papers on the protective value of paints on wood and metal surfaces have appeared during the year. J. S. Coye[83] states that the results of two years' exposure under normal conditions show that coal-tar paints are worthless as protectors of steel. Gypsum and whiting, when exceeding 5% of the paint pigment, are harmful. Zinc chromate is the best pigment for steel paints and may be used to advantage with other ingredients—*e.g.*, ferric oxide.

H. A. Nelson[84] has investigated the durability of paints on wood and metal surfaces by a method of accelerated weathering. The effects of sunlight, rain, and mist were imitated by a mercury lamp and by a revolving spray and a water atomiser, a variable-speed electric fan serving to maintain the temperature at 50°–60° C. By this arrangement a cycle of exposure for twenty-four hours to the rays of the lamp, followed by cooling and exposure to water spray for a further twenty-four hours at 5°–10° C., was chosen as representing actual service conditions. On an average, comparable results were obtained on a series of paints in as many days under the above conditions as would be given in months under service conditions. The results showed that for complete loss of gloss and initial chalking among white pigments, lead-free zinc oxide was much superior to white lead and Titanox. The maintenance of an atmosphere with saturated moisture accelerated the loss of lustre and chalking. Of commercial paints intended for use as protective coatings for iron, both the combination of 83% of ferric oxide with 15% of zinc oxide, and 100% red-lead paint showed outstanding merit, maintaining gloss and inhibiting the formation of rust, as compared both with iron oxide paints reduced with various fillers and a reduced zinc oxide sublimed lead paint.

J. N. Friend[85] has reviewed the conditions of preservation of iron with paint and from his own observations concludes that dark paints are specially to be recommended for the protection of iron and steel exposed to daylight. His conclusions are supported by the results of tests carried out in North Dakota, U.S.A. The protective power of a paint depends on a number of factors in which the pigment and the medium all play a part. Friend points out that the influence of the percentage of pigment, *e.g.*, Deep Indian Red, must be considered; the maximum efficiency was obtained with about 60% of that pigment, whereas in the case of red lead the maximum efficiency was obtained with 80% of the pigment. From his observations it would appear that the point of maximum protective efficiency coincides with ease of working. With regard to the influence of scale on iron and steel, the cheapest method and the one best calculated to prolong the life of the metal is considered to be to paint structures while their scale is still on, after removing any loosely adherent flakes and rust. It is evident that the conclusions drawn from the three contributions are of considerable importance, but do not admit of wide generalisations. The function of the medium is not always fully appreciated, and that of the nature of the pigment is apt to be exaggerated. There is no doubt that the properties of the linoxyn are modified by the pigment which is present, and that the production of a stable and elastic variety of that comparatively water-resisting substance is an important consideration. The loss of gloss of a paint film is intimately connected with the properties of the medium, influenced by the properties of the pigment.

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[82] *Cf. J.*, 1922, 820A.
[83] *Iowa Eng. Expt. Statn. Bull.*. 1919, 54.
[84] Amer. Soc. Test. Mat., 1922.
[85] *J. Oil and Col. Chem. Assoc.*, 1922.

E. C. Bingham, H. D. Bruce, and M. O. Wolbach[86] have shown that by use of the plastometer all colloidal solutions exhibit a yield value. A simple paint is a colloid of non-polar type. The effect of temperature is to increase the mobility without affecting the yield value. Quite different is the behaviour of a colloid of polar type, represented by glue or nitrocellulose in acetone; here the yield value decreases in a linear manner if the temperature be raised, and passes through a zero value, or from a plastic material to a viscous liquid. The writer has observed marked yield values for black japans, and for certain other varnishes.

Reference has been made in former Reports to the work of E. C. Bingham and H. Green on the consistency of paints depending on yield value and mobility. J. E. Booge, E. C. Bingham, and H. D. Bruce,[87] using a modified plastometer, have shown that the "consistency," mobility, and yield value are not simply related, but simple correlation was shown in nearly all cases examined. The clearest and most simple relationship was obtained by plotting the ratio of mobility and yield value against "consistency." The term "consistency" was expressed in an empirical notation of units, paints on the thick side being represented by the units 1, 2, 3, etc.

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[86] *J. Ind. Eng. Chem.*, 1922, **14**, 1014.

[87] Amer. Soc. Test. Mat., 1922; *J.*, 1922, 599A.

and on the thin side by —1, —2, —3, etc., the best painting consistency being designated as zero. The importance of such work cannot be over-estimated, and it is to be regretted that no simple relationship has been established between viscosity, yield value, and "consistency."

In last year's Annual Report the new Pfund colorimeter for white pigments was described, in which the principle of multiple reflections was adopted in order to accentuate departure from white, and a piece of ground optical glass was used as a non-selective reflecting surface. The measurement of the tinting strength of white pigments by the use of the Pfund colorimeter is proposed by J. H. Calbeck and C. P. Olanden[88]; a given amount of lampblack is ground with a definite quantity of white pigment using glycerin as medium, and the resulting loss in brightness measured on the colorimeter.

The relative merits of the application of paint by the brush and the spraying machine have been a matter of much controversy. After careful experiment the Society for Testing Materials[89] has expressed the opinion that the most efficient mode of painting is a combination of spraying and brushing, the paint being sprayed and then finished off by brushing. The two operations may be combined in one by use of a "spray brush," in which the paint is delivered in the form of a fine spray in a hollow brush.

Steinau[90] considers that the presence or absence of moisture must be regarded as a prime cause in the instability of lithopone to light, and the colour change is influenced by chlorine compound, especially zinc chloride. Lithopone containing chlorine yields metallic zinc in a finely-divided state when exposed to light, and for the preparation of lithopone stable to light there must either be complete exclusion of all chlorides or well-regulated control in their presence.

J. A. Hedvall[91] has shown that the bright yellow ferric oxide calcined at low temperatures and the red and purple varieties produced at higher temperatures are always crystalline, independent of the method of formation. D. Tyrer[92] describes a method for the manufacture of a red oxide of iron pigment by the digestion of galvaniser's waste liquor with scrap iron. Manganese violet,[93] prepared from manganese peroxide fused with phosphoric acid or ammonium phosphate, may be given a bluer tint by the introduction or iron compounds. R. O. Neal and G. Perrot[94] have given a valuable summary of the mode of manufacture of carbon black, pointing out the great influence of the temperature of combustion and regulation of the air supply on the yield and nature of the carbon black obtained.

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[88] Amer. Soc. Test. Mat., 1922; *J.*, 1922, 600A.

[89] *Oil and Col. Trades J.*, 1922, 793.

[90] *Chem.-Zeit.*, 1921, **45**, 1258; *J.*, 1922, 65A. *Cf.* E. Maas and R. Kempf, *Z. angew. Chem.*, 1922, **35**, 609; *J.*, 1922, 946A.

[91] *Oil and Col. Trades J.*, 1922, 791.

[92] E.P. 174,306; *J.*, 1922, 183A.

[93] G.P. 344,156; *J.*, 1922, 149A.

G. Bornemann[95] finds that Scheele's green is not acid copper ortho-arsenite $CuHAsO_3$, but a neutral arsenite $3CuAs_2O_3,xH_2O$.

C. A. Mitchell[96] gives a further account of graphites and other pencil pigments.

H. A. Gardner[97] communicates the results of the exposure of wood and metal test panels after three years' exposure at Atlantic City, U.S.A. Paints made on a basis of American vermilion (basic lead chromate) show remarkable protective qualities. As a medium for aluminium and zinc paints, boiled linseed oil is superior to spar varnish, which in turn is superior to collodion solutions. In the case of white paints he states that antimony or titanium oxide with zinc oxide give better results than when mixed with lead oxide.

In the analysis of pigments S. Glasstone[98] gives a direct iodometric method for the estimation of lead peroxide; A. Bonis[99] contributes a volumetric method for the estimation of red lead, and B. Paxton[100] a rapid volumetric process for the analysis of basic lead sulphate.

VARNISHES.

The effect of heat on the acidity and iodine values of copals during the process of "running" has been investigated by F. H. Rhodes and H. F. Johnson.[101] The copals selected were Congo, East India, and Manila, together with pontianak and kauri. The acidities were determined after heating the resins to 300°, 350°, and 390° C. In every case a decrease in acid value was observed. The iodine value of Congo copal diminished whilst that of East India copal was raised; the iodine values of the other resins were slightly higher at 300° C. but lower at higher temperatures. There is no apparent relation between the changes in the iodine value and acid value and the loss in weight on heating. The Congo copal used had an abnormally high acidity. The results are in general agreement with those of earlier investigators.

"Supercentrifugal force" and its application to the clarification of varnishes and the dehydration of oils by means of the Sharples supercentrifuge are discussed by H. Keable.[102]

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[94] *U.S. Bur. Mines Bull.*, 192, 1922.

[95] *Z. anorg. Chem.*, 1922, **124**, 36; *J.*, 1922, 946A.

[96] *Analyst*, 1922, **47**, 379; *J.*, 1922, 826A.

[97] *Circ.* 153, *Paint Manufrs. Assoc. U.S.*; *J.*, 1922, 946A.

[98] *Chem. Soc. Trans*, 1921, **119**, 1997.

[99] *Ann. Falsif.*, 1922, **15**, 157; *J.*, 1922, 557A.

[100] *Chem. and Met. Eng.*, 1922, **26**, 989; *J.*, 1922, 509A.

[101] *J. Ind. Eng. Chem.*, 1922, **14**, 279; *J.*, 1922, 380A.

[102] *J. Oil and Col. Chem. Assoc.*, 1922, **5**, 2.

H. Wolff and C. Dorn[103] have investigated the causes of turbidity in resin varnishes. If lead resinate be used in the manufacture of a linseed-oil varnish the precipitate is largely lead stearate, a result which has been known for a long time. Wherever free fatty acids are present they will react to produce lead salts with the liberation of an equivalent amount of resin acids. Varnishes containing manganese resinate remained clear. The insoluble lead salts contain small quantities of lime and silica, due no doubt to traces of "foots" still remaining in the varnish-oil. Repeated tests show that linseed oil, which has not had its mucilage removed, does not become as turbid on the addition of lead-drier as a purified oil; this is evidently due to the protective colloidal action of the mucilaginous matter which constitutes the "break." The fact that the presence of fused resinates, having an excess of resin, reduces the tendency to become turbid is, in the opinion of the writer of this Report, due to the acidity of the mixing, because reduction of acidity always tends to reduce the lustre even without the production of any precipitate.

H. Wolff[104] considers that "sanding" during storage of varnish is due to the growth of a crystalline deposit of lime and drier compounds caused by rapid and severe atmospheric changes. He also describes an apparatus[105] for the testing of hardness of varnish films. The varnish test-plate is moved at a definite rate, so that it comes in contact with a knife-edge which is loaded with known weights. A number of "cuts" are made at varying loads and compared. By substituting a strip of tinned iron in place of the knife-edge and taking obesrvations at loads slightly above zero, the progress of drying of the varnish surface can be observed by the adhesion or otherwise of the resting edge. In the comparison of the colour-intensity of varnishes H. Wolff recommends a Hellige colour-meter; the apparatus may be used on dried varnish films so that its practical value is greater.[106]

H. C. P. Weber[107] calls attention to the importance of thoroughly storing insulating varnishes which undergo decomposition during drying due to oxidation in order to remove volatile acidic substances of low electrical resistance which otherwise may accumulate and cause breakdown.

F. P. Ingalls[108] considers that specifications for varnishes based on chemical composition of varnishes are futile. Practically all the physical properties except durability can be quantitatively measured. The kauri reduction test gives reliable information on the durability of varnishes. Ingalls' conclusions are generally correct, although there is doubt as to the quantitative measurements of all the physical properties. The kauri reduction test is essentially for elasticity and may give satisfactory results in America, but it could not be relied on alone for varnishes exposed to the climatic conditions of the British Isles.

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[103] *Farben-Zeit.*, 1921, **27**, 26.

[104] *Ibid.*, 1922, **27**, 1047.

[105] *Ibid.*, 1922, **27**, 2555; *J.*, 1922, 558A.

[106] *Ibid.*, 1921, **27**, 415.

[107] *Trans. Amer. Electrochem. Soc.*, 1922, 89; *J.*, 1922, 867A.

[108] *Chem. and Met. Eng.*, 1921, **25**, 595.

H. A. Gardner, P. C. Holdt, and E. Bielouss[109] have investigated the rate of evaporation of thinners from "short oil" and "long oil" varnishes thinned with different varieties of volatile solvents, *e.g.*, turpentine, mineral hydrocarbons of varying boiling points, coal tar naphtha, etc., and have shown that the rate of evaporation is inversely proportional to the boiling point, as would be expected, and independent of the type of hydrocarbon. The hygrometric state of the surrounding atmosphere has no influence on the rate of evaporation from either paint or varnish film, and the highest viscosity of the finished product is obtained by the use of turpentine, whilst petroleum hydrocarbons give the lowest values. The statement that turpentine and solvent naphtha act as diluents without effecting any changes in dispersion, whereas petroleum hydrocarbons produce an alteration in structure by causing coalescence, does not seem convincing in view of the comparatively high viscosity of turpentine and the nature of the residue left on evaporation of solvent naphtha.

C. D. Holley[110] points out that the humidity of the air during the stoving of varnishes influences the time of drying, the character of the film, and sometimes the shade of the finish of lighter colours, so that the humidity must be kept constant at an optimum percentage.

H. A. Gardner and P. C. Holdt[111] have reviewed the methods for the determination of the consistency of varnishes, both for factory comparison and for expression of results in absolute units. The authors conclude that the plastometer of Bingham, and the MacMichael and Doolittle torsional viscosimeters are the only reliable instruments for determining viscosities of varnishes possessing the advantage of higher accuracy and greater ease in furnishing absolute results. From what has been mentioned in a previous paragraph the plastometer is, in the opinion of the writer, of great value, and the modified form of the apparatus gives rapid and reliable results for factory purposes.

A modification of the falling sphere viscosimeter is well worthy of attention, and gives results which can be expressed in poises.

F. S. Goucher and H. Ward[112] have worked out a relationship between the thickness, *t*, of a layer of varnish or enamel on a flat surface coated by dipping, and withdrawing at a known velocity, v, the varnish or enamel having viscosity, η, and density, ρ. $t^2=2v\eta\ \rho g$, where g=gravity constant. If the solid is a fine wire of radius r, the surface tension is dominant, and gravity negligible. If γ is the surface tension the relation must be of the form $\frac{t}{r}=f\left(\frac{\eta v}{\gamma}\right)$. It was found that $f\left(\frac{\eta v}{\gamma}\right)$ is of the form $4{\cdot}8\ \frac{\eta v}{\gamma}$ in c.g.s. units.

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[109] *Circ.* 141, *U.S. Paint Manuf. Assoc.*, 1921 ; *J.*, 1922, 904A.
[110] *Chem. and Met. Eng.*, 1921, **25**, 873.
[111] *Circ.* 127, *U.S. Paint Manuf. Assoc.*, 1921 ; *J.*, 1922, 905A.
[112] *Phil. Mag*, 1922, **44**, 1002.

J. B. Coleman and P. Bilham[113] have investigated the physical and chemical properties of dekalin in order to determine its suitability as turpentine substitute. Chemically dekalin consists primarily of a mixture of 20% of tetrahydronaphthalene and 80% of decahydronaphthalene. Its rate of evaporation prohibits its use for quick-drying varnishes, but for paints and slow-drying varnishes it is no disadvantage, as the drying action continues all the time the dekalin is evaporating, owing to its oxygen-carrying properties, which are peculiar to the tetrahydro-compound and not to the deca variety.

The numerous references which have been made to the circulars of the United States Paint Manufacturers' Association, and the many and interesting results contained therein, show the great advantage of a research station to the industry, where not only problems relating to the difficulties of the day are dealt with, but also investigation of fundamentals is being carried out, which no doubt will lead to the discovery of new properties of great value.

H. Vollmann[114] has endeavoured to simplify the detection of lead, manganese, and cobalt in drying oils and varnishes. Any methods which will enable the presence of these metals to be detected in the varnishes without incineration will be a great boon. It must be remembered that in varnishes the percentages of manganese and cobalt are very small compared with those of lead, and although Vollmann's method for the detection of lead works satisfactorily yet the methods for manganese and cobalt are not reliable unless the varnish has been incinerated. If the percentages of manganese or cobalt are comparatively high, as in terebines, satisfactory results are obtained. The methods given in the paper, which are rather complicated, are quite satisfactory when the ash is examined. The use of α-nitroso-β-naphthol or ammonium thiocyanate gives satisfactory results. The test for manganese is a modification of the method of Sacher,[115] which is always reliable.

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[113] *Chem. Age*, 1922, **7**, 554 ; *J.*, 1922, 904A.

[114] *Farben-Zeit.*, 1922, **27**, 1943 ; *J.*, 1922, 381A.

[115] *Ibid.*, 1920, **25**, 1309.

INDIA-RUBBER.

By B. D. W. Luff, F.I.C.,

Research Chemist, North British Rubber Company, Ltd., Edinburgh.

A survey of the scientific literature published during the past year should serve to dispel any lingering doubts regarding the claim of rubber manufacture to be considered as a chemical industry.

That the manufacturers themselves appreciate the position is reflected in the nature of the papers delivered before the Institution of Rubber Industry, a recently-formed organisation which derives its chief support from manufacturing concerns. The majority of these communications have been concerned with various scientific aspects of rubber manufacture, and have in most cases been read by well-known chemists connected with the industry.

Further evidence of the sympathetic attitude of the manufacturers towards scientific advancement is afforded by the formation of the British Rubber and Tyre Manufacturers' Research Association. Inaugurated some three years ago, work was originally carried on in temporary quarters in University College, London. Commodious premises were ultimately secured at Croydon, and these have now been splendidly equipped as research laboratories, being formally opened by Lord Colwyn in July.

Rubber again finds a place in the series of publications dealing with colloid chemistry and its general and industrial applications, the British Association for the Advancement of Science having recently issued the Fourth Report, to which H. P. Stevens has contributed the section on rubber, the same author having compiled a bibliography on the subject for the First Report, published in 1917.

Statistics.

Attention has been directed in previous reports to the grave situation which has gradually developed in regard to the output of raw rubber, which has been steadily overtaking the consumption, until an actual surplus production has resulted, stocks at January 1st, 1922, being estimated as 110,000 tons over actual requirements.[1]

Such a state of affairs is fraught with serious consequences, alike to the planting companies, the Colonial Governments, and the rubber manufacturers, and an attempt was made to meet the position by the Rubber Growers' Association, the bulk of whose members agreed to a voluntary reduction in output, the effect of which is reflected in the returns for 1921, as compared with those of the preceding year.[2]

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[1] *India Rubber J.*, 1922, **63**, 907.

[2] *Loc. cit.*

Production of Crude Rubber.

	Plantation. Tons.	Wild. Tons.	Total. Tons.
1920	335,000	35,000	370,000
1921	260,000	22,000	282,000

The Dutch planters, whose estates furnish approximately 25% of the total production of cultivated rubber, could not be induced to co-operate in such a scheme of restriction, and the situation was further aggravated by a proportion of the British estates refusing to continue their adherence to the arrangement. The Colonial Secretary, however, appointed a committee, of which Sir James Stevenson was chairman, to investigate the position in British Colonies and Protectorates. In the first report,[3] issued in June, 1922, the situation was carefully reviewed and two alternative schemes propounded, but the committee was unable to recommend the adoption of either proposal until the attitude of the Dutch planters was known. Notwithstanding the subsequent refusal of the Netherlands Government to introduce legislation to restrict the production of rubber in their Colonies, the Stevenson Committee in October issued a supplementary report[4] in which it recommended the application of a scheme of Government intervention in Ceylon, the Malay States, and the Straits Settlements.

Briefly the report advocates the imposition of a scale of export duties, varying according to the relation which the amount exported from any particular estate bears to the standard production, which, with certain modifications, is taken as the output of the estate for the twelve months, November 1st,1919, to October 31st, 1920.

If the amount exported over a period of twelve months does not exceed 60% of the standard production, the minimum export rate decided upon shall be applied. If a greater percentage than 60 is exported the duty imposed on the total export shall be on the following scale :—

	Duty per pound over all. s. d.
Not exceeding 65% of standard production	0 4
Over 65% but not exceeding 70%	0 5
„ 70% „ „ „ 75%	0 6
„ 75% „ „ „ 80%	0 7
„ 80% „ „ „ 85%	0 8
„ 85% „ „ „ 90%	0 9
„ 90% „ „ „ 95%	0 10
„ 95% „ „ „ 100%	0 11
„ 100%	1 0

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[3] *Loc. cit.*

[4] *Ibid.*, 1922, **64**, 639.

The percentage of the standard production allowed at the minimum export rate, 60% on the initiation of the scheme, will be adjusted from time to time according to the improvement or otherwise in the rubber situation. The price of standard quality smoked sheet in the London market is to be taken as the factor for determining this, and when, for example, the price has averaged not less than 1s. 3d. per lb. for three months the percentage of production allowed at the minimum rate will be raised by 5% for the next quarter.

The effect of these duties will be to encourage estates to keep production and therefore the duty low, as the rubber will command only the standard market price, whatever the duty paid.

This scheme, recommended in October, was approved by the Colonial Office and was immediately adopted by the Colonial Legislatures and put into force in Ceylon, Malaya and the Straits Settlements, the new duties taking effect on November 1st.

The rubber market was affected as soon as the supplementary report was issued, the price of smoked sheet steadily rising from 9d. per lb. on October 9th, to 1s. 2d. on December 11th.

The report recommends that part of the revenue obtained by the application of the export duties be set aside for the benefit of the plantation industry, either in the direction of fostering research or investigating new uses for rubber.

The Dutch planters are, of course, unaffected by these restrictive measures and will benefit by an increased price for raw rubber while being under no obligation to limit their output.

RUBBER LATEX.

Although S. Peel in 1791[5] patented the use of rubber "in its native fluid state" for waterproofing cotton, paper, etc., latex has hitherto been received in this country only in small quantities, and, indeed, F. Kaye[6] has expressed doubts whether 1000 gallons of latex in all has been shipped from the producing countries during the past 100 years. Recently, however, there has been a tendency to consider the possibilities of using latex in the making of certain rubber goods. This was stimulated by the discovery of F. Kaye[7] who found that latex could be successfully employed in the manufacture of paper. Full particulars of the process were published recently by the inventor,[8] and it would seem that the discovery will lead to important developments in the art of paper-making. The latex is introduced during the beating process, a coagulating agent being added towards the end of this operation. The rubber-impregnated paper may, if desired, be vulcanised, preferably by the Peachey process, but it is not yet certain whether this is to be regarded as necessary. The introduction of quite small percentages of latex has a marked effect on the strength of the paper produced, although the figures originally published have been somewhat modified by more recent investigation.[9]

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[5] E.P. 1801.

[6] *India Rubber World*, 1922, **67**, 75. Shipments have been made on a large scale in recent months; *e.g.*, the amounts of rubber latex received at New York during August and November, 1922, were 750,000 lb. and 426,000 lb., respectively.

[7] *J.*, 1921, 690A.

[8] *India Rubber J.*, 1922, **64**, 435; *J.*, 1922, 806A.

A certain amount of apprehension has been expressed by some paper makers, who have always regarded the presence of rubber in paper as undesirable. This attitude is probably due to a lack of appreciation of the fact that the rubber is to be introduced in the form of latex, and not as coagulated rubber. The process is being quickly developed industrially, and an enterprising trade journal, alive to its possibilities, used some of the paper thus produced for the covers of a number of issues.[10]

Other proposed applications of latex are in the preparation of rubberised fabric[11] or thread,[12] in making spongy material,[13] in the manufacture of adhesives by mixing with casein, glue, etc.,[14] and in the preparation of roadways.[15] H. P. Stevens has shown[16] that it is not possible to vulcanise rubber while in the form of latex by successive treatment with hydrogen sulphide and sulphur dioxide as the gases merely dissolve in the serum and react there with production of sulphur in an inactive form. It would be interesting to know whether vulcanisation could be brought about by working at high pressures.

The success with which latex could be shipped from the estates to the manufacturing countries would, to a great extent, depend on whether or not the danger of premature coagulation could be eliminated. The use of ammonia as a preventive agent was patented as far back as 1853,[17] and F. Kaye has stated that he has found latex preserved by ammonia arrive in satisfactory condition.

Although the possibility of premature coagulation is a problem which has to be faced on the estates, reagents which may well suffice for short periods such as obtain under these conditions might not be equally suitable for use when the latex has to be transported long distances. However, a number of consignments have come

[9] *India Rubber J.*, 1922, 938
[10] *Ibid.*, 471.
[11] P. Bristain and Griffiths Bros. & Co. E.P. 184,578 ; *J.*, 1922, 827A.
[12] E. Hopkinson, U.S.P. 1,411,786 ; *J.*, 1922, 383A.
[13] P. Schidrowitz and H. A. Goldsbrough, E.P. 1111, 1914 ; *J.*, 1915, 624.
[14] Schidrowitz, E.P. 166,731 ; *J.*, 1921, 668A.
[15] P. H. Clark, *Le Caoutchouc et la Gutta Percha*, 1922, 11,486.
[16] *Bull. Rubber Growers' Assoc.*, 1922, 4, 386 ; *J.*, 1922, 772A.
[17] W. Johnson, E.P. 467, 1853.

to this country recently without mishap, and there does not seem to be any reason for anticipating trouble in this respect. In this connexion H. P. Stevens[18] has recently published the results of tests with a number of preservatives, such as ammonia, sodium fluoride, sodium silicofluoride, cresol preparations, caustic soda, and pyridine; the best results were obtained with ammonia and caustic soda, and it is suggested that the latter would be suitable for most purposes. A number of patents have been granted to S. C. Davidson during the last few years for the use of sodium phenoxide as preservative.

In the event of the shipment of latex becoming common, some means will have to be found to arrive at the rubber content, and it has been pointed out by H. C. Pinching[19] that the Metrolac[20] form of hydrometer is not suitable for general use in this connexion. H. P. Stevens[21] tentatively proposes the determination of total solid left on evaporation as the most suitable method of evaluation.

Preparation of Raw Rubber.

The fact that cultivated rubber is prepared by a method of coagulation differing essentially from that which obtains in the case of Para rubber has led to various attempts to secure a more complete parallelism on the plantations. In a recent patent[22] a method is described in which the latex distributed over a travelling endless band is exposed to the action of a current of smoke inside a suitable chamber. In another process[23] the latex, previously treated with a reagent such as ammonia, or saponin, in order to prevent coagulation, is sprayed into a chamber heated to 93° C., through which a stream of air or other gases is passing. It is claimed that the rubber prepared in this way has improved tensile properties and a high rate of cure would also be expected, H. P. Stevens having shown[24] that rubber prepared by evaporating latex vulcanises much more rapidly than that resulting from ordinary coagulation.

That the method of preparation influences the properties of the rubber produced has long been realised and much work continues to be done in this connexion. The effect of the proportion of coagulant on the rate of cure of the resulting rubber has been investigated by H. P. Stevens,[25] who concludes that using the minimal proportion of coagulant a more rapidly curing rubber is obtained, the rate of cure decreasing with increasing proportion of coagulant, this effect being more pronounced in the case of sheet than crêpe rubber. The same author,[26] by using less than the usual amount of acetic acid, has induced partial coagulation and has found that the rubber so produced has a slightly higher rate of cure, and an appreciably higher breaking strain than the fraction obtained by subsequently completing the coagulation. Naturally fermented "toddy,"[27] crude pyroligneous acid from the distillation of coconut shells,[28] and Boehringer's powder have been examined as coagulating agents. The last-named substance, which consists of aluminium lactate, gives rubber which is of inferior tensile strength and lower rate of cure than normally prepared rubber.[29]

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[18] *Bull. Rubber Growers' Assoc.*, 1922, **4**, 457; *J.*, 1922, 868A.

[19] *Rubber Age*, 1922, **3**, 446.

[20] *Ann. Repts.*, 1919, **4**, 317; 1920, **5**, 334.

[21] *Ibid.*, 448.

[22] H. A. Wickham, and Roa, Ltd., E.P. 177,262; *J.*, 1922, 383A.

[23] E. Hopkinson, E.P. 157,975, 157,978; *J.*, 1922, 677A.

[24] *J.*, 1922, 326T.

[25] *Bull. Rubber Growers' Assoc.*, 1922, **4**, 134; *J.*, 1922, 335A.

Apart from the method of treatment, variations in the rubber may be traced to the latex itself, and O. de Vries[30] has shown that whereas uniform properties are exhibited by rubber from trees between six and fifteen years old, in the case of younger trees the rubber content of the latex is often low and the tensile strength of vulcanised samples inferior to that of rubber from the older trees.

The variability of the yield of rubber obtained from different trees has been previously noted by G. S. Whitby[31] and O. de Vries,[32] and the latter has brought forward further evidence of the extent to which this may occur; twelve trees on one estate gave yields of rubber varying from 9·6 to 68·4 g. per day, the rubber content of the latex being from 25 to 46%. It was also found that there were wide variations in the solution viscosity of the rubber from the different trees, and that the values obtained from the same tree were not always constant. The rate of vulcanisation and the "slope," however, did not show marked differences, but in certain trees the tensile strength was consistently low.

The liability of mould growths to occur on sheet rubber has been dealt with in a previous report,[33] and this question now appears to be receiving serious attention. H. P. Stevens, who points out that the smoking of sheet rubber is not sufficiently fungicidal to prevent the development of mould, has found[34] that formalin, probably on account of its volatile nature, is also ineffective, but sodium silicofluoride when introduced into the latex before coagulation gives satisfactory results. Later experiments[35] indicate that the addition of 0·06% to a standardised latex is sufficient to inhibit mould growth, although there is still a possibility of its occurrence if the sheets are packed in a wet condition. Rubber which has been treated with sodium silicofluoride in this manner usually exhibits a slightly higher rate of cure than the untreated rubber.

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[26] *Bull. Rubber Growers' Assoc.*, 1922, **4**, 196; *J.*, 1922, 475A.

[27] H. P. Stevens, *ibid.*, 1922, **4**, 197.

[28] *Ibid.*, 1921, **3**, 245.

[29] W. Spoon, *Comm. Central Rubber Station, Buitenzorg*, 1922, No. 29, 140; *J.*, 1922, 827A.

[30] *Ibid.*, 1922, No. 31, 296; *J.*, 1922, 827A.

[31] *Ann. Repts.*, 1919, **4**, 313.

[32] *Ibid.*, 1920, **5**, 334.

[33] *Ibid.*, 1920, **5**, 337.

[34] *Bull. Rubber Growers' Assoc.*, 1922, **4**, 132; *J.*, 1922, 335A.

Although mouldy sheets are regarded with disfavour by brokers, there is little or no evidence to indicate that the rubber is affected detrimentally by the presence of these growths ; at the same time it has been stated[36] that very pronounced mould development does sometimes give rise to considerable variation in the rate of cure.

The extent to which appearance influences buyers of rubber is further instanced in the case of smoked sheet, the colour of which is frequently regarded as a criterion, but H. P. Stevens[37] on examining a range of samples varying from a very light to a dark colour, was unable to detect any difference in the tensile properties after vulcanisation.

In view of the scientific method pursued by those interested in the production of satisfactory grades of raw rubber as is abundantly evidenced by the foregoing, it comes as an anti-climax to learn that perhaps the chief defect in rubber as it reaches the manufacturers is the presence of wood splinters and dirt.[38] A symposium of the views of American manufacturers has recently appeared,[39] showing the prevalence of this defect, which is further emphasised in a communication by B. D. Porritt[40] summarising the views of British manufacturers regarding the merits and defects of plantation rubber. It is gratifying to learn that the plantation managements may be exonerated from blame in this matter, as, according to H. P. Stevens,[41] the bulk of such contamination arises during unpacking, sampling, and repacking at the wharves.

The use of the microscope in detecting faults such as mould, air bubbles, "rust," in raw rubber, has been referred to by H. Sutcliffe.[42]

CHEMICAL PROPERTIES AND CONSTITUTION.

Attempts have frequently been made to hydrogenise caoutchouc molecule by reduction in presence of a suitable catalyst, but hitherto only negative results have been obtained. By treatment with hydrogen at 270° C. in presence of a platinum catalyst and working at a pressure of 100 atmospheres H. Staudinger and J. Fritschi[43] have succeeded in preparing a hydrocaoutchouc having the empirical formula C_5H_{10}. This compound forms a non-elastic mass, but the colloidal nature still persists. It is dissolved by benzene, ether, and chloroform, but is insoluble in alcohol and acetone. While unattacked by bromine under ordinary conditions, a reaction takes place in sunlight with formation of a rubber-like mass. It is interesting to note that the substance is not capable of vulcanisation, which supports the view that chemical combination at the double bonds is necessary to bring about this change. It is concluded that the rubber molecule consists of isoprene molecules condensed in a long closed chain.[44]

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[35] *Bull. Rubber Growers' Assoc.*, 1922, **3**, 227, 331 ; *J.*, 1922, 510A, 721A.

[36] H. P. Stevens, *J.*, 1922, 66A.

[37] *Bull. Rubber Growers' Assoc.*, 1921, **3**, 521 ; *J.*, 1922, 110A.

[38] *Ann. Repts.*, 1921, **6**, 358.

[39] *India Rubber World*, 1922, **66**, 602.

[40] *India Rubber J.*, 1922, **64**, 421.

[41] *Ibid.*, **64**, 825.

[42] *Ibid.*, **63**, 759.

From a study of the behaviour towards reducing agents of the dihydrochloride obtained by the action of hydrogen chloride on a chloroform solution of caoutchouc, C. Harries and F. Evers[45] have been led to the belief that the chain consists of eight isoprene nuclei forming a 32-atom ring.

An interesting investigation of the action of sulphuric acid on solutions of rubber in organic solvents has been carried out by F. Kirchhof,[46] who finds that the final product of the reaction is similar to that resulting from oxidation; the preparation of a crystalline phenylhydrazone of one of the degradation products is noteworthy.

As might be expected, the synthesis of rubber does not now command much attention, although the question is not entirely neglected. H. O. Traun[47] has patented a method for the preparation of diolefines which consists in heating together in the presence of catalysts molecular equivalents of acetylene and ethylene hydrocarbons; the reaction products may be polymerised by suitable means, giving rubber-like substance together with compounds which may serve as turpentine substitutes. In a similar manner[48] acetylene hydrocarbons may be caused to react with hydrogen halide and the product polymerised to give halogenated compounds similar to those resulting from the action of chlorine on rubber,[49] and employed as varnish under the name of Duroprene; the photo-polymerisation of vinyl chloride has also been studied by J. Plotnikow.[50]

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[43] *Helv. Chim. Acta*, 1922, **5**, 785; *J.*, 1922, 868A.

[44] *Cf.* S. S. Pickles, *J. Chem. Soc.*, 1910, 1085.

[45] *Wiss. Veröffentl. Siemens-Konzern*, 1921, **1**, 87; *J.*, 1922, 23A.

[46] *Kolloid-Zeits.*, 1922, **30**, 176; *J.*, 1922, 335A.

[47] E.P. 156,116; *J.*, 1922, 436A.

[48] E.P. 156,117; *J.*, 1922, 436A.

[49] S. J. Peachey, E.P. 1894, 1915; *J.*, 1916, 479.

[50] *Z. wiss. Phot.*, 1922, **21**, 117; *J.*, 1922, 261A.

VULCANISATION.

The varied nature of the processes by which the change known as vulcanisation may be induced has been well illustrated in a paper by P. Schidrowitz,[51] and since this was written a further addition to the list must be made. C. W. Bedford and L. B. Sebrell[52] in an investigation of the reactions taking place between sulphur dioxide and hydrogen sulphide in a cooled benzene or carbon bisulphide solution, have succeeded in isolating an active form of sulphur, which they consider to be trithio-ozone. This active sulphur if introduced into a cooled cement will cause vulcanisation to occur at low temperatures, and the authors explain the reactivity of the sulphur liberated in the Peachey process by assuming it to be in this form. It is pointed out that the fact that sulphur is "nascent" does not necessarily imply that vulcanisation will occur, as the sulphur liberated by the interaction of nitroso derivatives and hydrogen sulphide does not act in this way.

These authors have also shown that zinc persulphides are capable of acting as vulcanising agents, the time required for curing being shorter than with ordinary sulphur.

The extent to which the accessory substances in raw rubber influence the progress of vulcanisation has been the subject of numerous investigations, and, in order to determine whether the effect varies according to factors such as the age of the tree from which the rubber is obtained, G. Martin and F. L. Elliot[53] have examined a series of samples of sheet and crêpe rubber. Rubber from trees ten years old, whether in the form of sheet or crêpe, had a somewhat higher rate of cure than that from trees twenty years old, and in all cases the sheet rubber vulcanised faster than the crêpe.

The authors were able to confirm the results of O. de Vries,[54] who has shown that as the time of cure decreases the vulcanisation coefficient at standard cure increases, in contradistinction to what is observed in the case of organic accelerators where a reduction in the time of cure is accompanied by a decrease in the vulcanisation coefficient. Resins extracted from crêpe, sheet, and slab rubber were added to unextracted crêpe rubber in a mixing of the composition, crêpe rubber 88, sulphur 10, extracted resin 2, but little effect was noted on the rate of cure excepting in the case of the slab resin, where a marked accelerating action resulted.

The reactions between rubber and sulphur in various solvents at 120° C. have been studied by F. Boiry,[55] working on the lines indicated by H. P. Stevens,[56] and gels giving residues having high coefficients of vulcanisation have been obtained. In solutions containing 2% of rubber and 1% of sulphur masses were produced having combined sulphur contents, varying from 15 to 30·5%, according to the solvent employed.

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[51] *India Rubber J.*, 1922, **63**, 65.
[52] *J. Ind. Eng. Chem.*, 1922, **14**, 29; *J.*, 1922, 262A.
[53] *J.*, 1922, 226T.
[54] *J. Ind. Eng. Chem.*, 1921, **13**, 1133; *J.*, 1922, 23A.
[55] *Comptes rend.*, 1922, **175**, 102; *J.*, 1922, 640A.

There are several processes available for preparing vulcanised gels, which may find application in the form of cements for uniting surfaces such as leather or rubber,[57] for proofing paper, leather, wood, etc.,[58] or for making rubber articles by "wet moulding."[59]

COMPOUNDING INGREDIENTS.

Although certain specific effects of various ingredients employed in preparing rubber mixings have long been familiar to those engaged in the industry, it is only within the last two or three years that systematic investigations have been undertaken, a comprehensive study by W. B. Wiegand[60] having doubtless stimulated research in this direction. The varied properties which a material may confer on a vulcanised rubber into which it has been incorporated are well illustrated by H. W. Greider[61] in studying light magnesium carbonate. This material is regarded as of peculiar interest as, owing to the uncertain nature of the supply of "gas black," some other light reinforcing filler should be available for use in the event of gas black being unobtainable. The light carbonate is generally regarded as having the composition $4MgCO_3.Mg(OH)_2,5H_2O$, but the author finds that analyses more nearly correspond to $11MgCO_3,3Mg(OH)_2,11H_2O$, although differences occur according to the conditions of preparation. The properties were examined by introducing various proportions into a basic mixing containing litharge similar to that employed by Wiegand. It was found that the material behaved as a typical reinforcing pigment as evidenced by the stress-strain curves, and when the mixing contained 20 volumes of filler per 100 volumes of rubber, the stress-strain relationship was nearly in accord with Hooke's law. The tensile strength increased by the addition up to 9 vols. of filler, and then decreased until at 20 vols. the strength equalled that of the basic mixing; the ageing properties were improved by addition of from 6 to 9 volumes of the carbonate. The hardness of the vulcanised rubber was greater than that obtained by using zinc oxide, but less than that obtained by means of gas black. The permanent set, however, was high and increased up to addition of 20 vols., subsequently decreasing owing to the low extensibility of such a sample. The high permanent set is said to be characteristic of crystalline compounds, and the author makes the interesting suggestion that, by applying the principles of colloid chemistry in the precipitation a less crystalline product should result in which the undesirable properties of the magnesium carbonate will be less conspicuous.

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[56] *J.*, 1921, 186T.
[57] S. J. Peachey, E.P. 176,073; *J.*, 1922, 302A.
[58] S. J. Peachey, E.P. 177,566; *J.*, 1922, 383A.
[59] F. C. Jones, E.P. 186,691.
[60] *Ann. Repts.*, 1920, **5**, 343.
[61] *J. Ind. Eng. Chem.*, 1922, **14**, 385; *J.*, 1922, 425A.

The superiority of "carbon black"[62] over ordinary lampblack is generally accepted, and further evidence is afforded by the work of E. Marckwald and F. Frank,[63] who, with a mixture containing rubber 55, black 25, sulphur 5, litharge 5, and zinc oxide 10 parts by weight, showed that the vulcanised product possessed greater resistance to tearing and higher breaking strength in the case where carbon black was employed, but that the lampblack samples possessed greater resilience.

In the course of experiments on the asphaltic compound known as "mineral rubber," C. O. North[64] has found that its incorporation up to 40 volumes per 100 volumes of rubber does not affect the form of the stress-strain curve. The breaking load increases up to 7 volumes, and then falls off slightly, but it is concluded that up to 15 volumes the introduction of mineral rubber is advantageous from many points of view. The chief defect of this material, however, lies in the slowness of recovery from deformation of the stocks into which it is introduced; this means that in the case of a revolving tyre the depression caused by contact with the road surface does not disappear before the next contact, and as a result flattening occurs.

The importance of the fineness of division of compounding ingredients is now so widely appreciated that it is not surprising to find a number of communications dealing with methods for the determination of particle size. Although more properly belonging to the section dealing with pigments, brief mention may be made here of some of the more important communications which bear on the question as it affects the rubber industry.

H. Green[65] describes a method which, although perhaps not altogether novel, has the merit of being based on direct measurement. The pigment is prepared in such a manner as to allow a photomicrograph to be taken at a known magnification. The negative is placed in a stereopticon, and an image thrown on a screen, so that the total magnification will be 20,000 to 25,000 diameters, the image of each particle being measured by means of a rule. The screen is divided into small squares so as to facilitate counting and in this way each particle is measured and an average size determined.

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[62] *Ann. Repts.*, 1919, **4**, 324.

[63] *Gummi-Zeit.*, 1922, **36**, 1459; **37**, 5; *J.*, 1922, 906A

[64] *India Rubber World*, 1921, **65**, 191; *J.*, 1922, 224A.

[65] *J. Franklin Inst.*, 1921, **192**, 637.

In comparing pigments for incorporation in rubber mixings, it would be interesting to know how the dispersion on the microscope slide compares with that obtained in the rubber mixing, and whether the pigment should be dispersed on the slide to its maximum extent, by adding some peptising agent such as soap solution.

Methods for determining particle size are referred to in a paper by A. D. Luttringer,[66] and, besides a description of Green's method, the methods of Dinwiddie and Vogt are outlined. In the former the pigments may be examined qualitatively by smearing on to a gramophone disc when particles adhere to the grooves; these are usually 0·001 inch deep, and have a radius of curvature of 0·004 inch. Examination in this manner gives a rough idea of the comparative size of different pigments, and a more accurate idea may be obtained by suspending a given weight of pigment in a suitable liquid, diluting largely, and determining the number of particles by means of the hæmacytometer in the manner adopted for counting the corpuscles in blood; from the number of particles the weight, and, knowing the density, the size of separate particles may be calculated.

W. W. Vogt's method[67] consists in dispersing a known weight of the pigment in a suitable liquid, *e.g.*, glycerin, and determining the height of a column necessary to obscure a given source of light. The method is based on the idea that the smaller the particles the greater will be the projected area interposed between the observer and the light, and, consequently, the less will be the height of the column of dispersed pigment necessary to bring about obscuration. While this method may be quite suitable for comparing samples of the same pigment, it may not afford a means of comparison between samples of different composition and different optical properties.[68]

An interesting review of the properties due to particle size has been given by A. A. Pollitt,[69] and W. M. Ames[70] has published some useful hints on photomicrographic methods.

Very little work on the chemical examination of pigments has been carried out, but a paper by A. Short and F. H. Sharpe[71] on the composition of golden sulphide of antimony is of interest. The authors have examined a range of products of various manufacturers, and in each sample have determined antimony, free sulphur, and calcium sulphate ($CaSO_4,2H_2O$). If the antimony is calculated as Sb_2S_4 it is found that in all cases the results add up to 100%, from which it is concluded that antimony is present as tetrasulphide Sb_2S_4, and not as a higher sulphide, or even as trisulphide.[72] They adopt Kirchhof's view that this tetrasulphide is antimony thioantimonate $Sb(SbS_4)$, but also suggest the possibility of its being a compound Sb_2S_3,Sb_2S_5, although it is not clear what is to be understood by this. It has been generally accepted that commercial samples contain a mixture of the trisulphide and pentasulphide, and, as D. F. Twiss points out,[73] even in the case of the samples examined there is no evidence to disprove the presence of a sulphide higher than the tetrasulphide admixed with trisulphide. Perhaps the most striking feature of the analyses quoted is the presence of such a high percentage of fixed sulphur, as it is rarely that samples are met with containing antimony combined with sulphur in the proportion corresponding with the formula Sb_2S_4

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[66] *Le Caoutchouc et la Gutta Percha*, 1922, 11,308.

[67] *India Rubber World*, 1922, **66**, 347.

[68] W. Feldenheimer, *Rubber Age*, 1922, **3**, 8.

[69] *Chem. Age*, 1922, **6**, 545.

[70] *Rubber Age*, 1922, **3**, 213.

[71] *J.*, 1922, 109T.

This was shown by B. D. W. Luff and B. D. Porritt,[74] and their figures have received confirmation at the hands of N. A. Shirk and N. R. Wilson,[75] who have examined a range of samples of English, French, and German manufacture in which the percentages of antimony trisulphide were 23·7, 73·7, 60·5, and those of antimony pentasulphide 8·8, 16·1, 19·2 respectively. If these figures are expressed on the basis of the antimony being present as tetrasulphide Sb_2S_4, the proportions of this become 16·1, 29·6, and 35·3%, the trisulphide being present to the extent of 16·4, 60·2, and 44·4%, respectively, whereas in the analyses quoted by Short and Sharpe the trisulphide is entirely absent.

Among other materials which have been proposed for incorporation into rubber mixings may be mentioned phenol-formaldehyde condensation products,[76] and that glue is now a recognised constituent is indicated by its inclusion in the American Chemical Society's official scheme of analysis and in the Bureau of Standards Circular No. 38 (4th Edition).

For the preparation of compounding ingredients in a fine state of division, the Plauson "Colloid mill" may ultimately prove valuable, although it remains to be seen whether the results obtained will justify such a procedure being adopted. In the event of gas black becoming scarce, as has been predicted, treatment of ordinary lampblack or charcoal in this apparatus might afford a suitable substitute.

[72] *Cf.* Kirchhof, *J.*, 1920, 721A.

[73] *J.*, 1922, 172T.

[74] *Ann. Repts.*, 1921, **6**, 378.

[75] *India Rubber World*, 1922, **66**, 612.

[76] A. Speedy and A. P. Crouch, E.P. 171,803; *J.*, 1922, 67A; H. Frood, E.P. 176,405; *J.*, 1922, 335A.

During the past year the India Rubber Regulations, 1922, have come into force, and as a result manufacturers have to adopt special precautions where litharge or other lead compound is employed, if the lead compound is present in any mixing to such an extent that 5%, calculated as PbO, is soluble in 0·25% hydrochloric acid. The actual solubility test is carried out on the dry material before incorporating with the rubber, and the result calculated on the weight of the finished batch of compounded rubber. Those mixings which contain more than 5% of soluble lead are classed as lead compounds and provision must be made for removal of dust containing lead at the point of origin, for a supply of overalls for workers, and mess-room accommodation, etc. While most of the larger firms had already taken such steps to safeguard the workers, a number of smaller firms could not readily comply with the Regulations, and as a consequence rubber already compounded with litharge is being supplied by certain manufacturers, as in this form no dust can arise and the material is not regarded as a lead compound.[77] Under the Regulations carbon bisulphide, benzene, carbon tetrachloride, and sulphur chloride are classed as dangerous compounds and special arrangements must be made where these are in use.

PHYSICAL PROPERTIES.

The increase in volume exhibited on stretching vulcanised compounded rubber, which was discovered by H. F. Schippel,[78] has been examined by H. Green,[79] who, by observation under the microscope, has confirmed Schippel's conclusion that the formation of vacuoles at the extremities of agglomerates of pigment particles is primarily the cause of this phenomenon. It is not yet certain whether the whole of the observed increase in volume is due to this cause, but Green has been able to obtain photomicrographs of a barytes mixing in which the elongated vacuoles at the ends of the particles are evident.

The somewhat high penetrability of rubber films to gases has gradually led to the conclusion that this is to some extent due to solubility of the gas, and not entirely to be explained by a simple process of diffusion. Experiments on the solubility of various gases in raw and vulcanised rubber have been carried out by C. S. Venable and T. Fuwa,[80] who exposed strips of the material in an atmosphere of the gas and determined the amount absorbed by direct measurement after exhaustion by means of a Töpler pump. The authors conclude that when rubber takes up a gas the process is one of true solution and not of adsorption. The diffusion of a gas through a rubber membrane takes place by solution of the gas on the one side and effusion of the dissolved gas into the atmosphere on the other side, the latter process being the chief factor determining the rate of penetration. The authors conclude, however, that there is a general relationship between the solubility of the gas and its relative rate of diffusion, but the actual structure of the gas molecule and the viscosity of the rubber may likewise have a marked influence.

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[77] *J.*, 1922, 325R.

[78] *Ann. Repts.*, 1920, **5**, 344.

[79] *J. Ind. Eng. Chem.*, 1921, **13**, 1029.

[80] *Ibid.*, 1922, **14**, 139; *J.*, 1922, 183A.

In making tests on ordinary breathing bags, A. C. Fieldner, S. H. Katz, and S. P. Kinney[81] have shown that rubber sheet $\frac{1}{16}$ in. thick was permeable to benzene or gasoline, but not to carbon monoxide or natural gas.

Considering that the phenomenon of blooming may be concerned with the solubility of sulphur in rubber, it is somewhat remarkable that little or no work has been done in this direction. The preliminary experiments of C. S. Venable and C. D. Greene[82] should therefore be of value, although the authors realise that their work is not by any means complete.

So far, the solubility of sulphur in rubber at 55°, 75°, 95°, and 140° C. has been determined by immersing in flowers of sulphur thin strips of rubber, either raw or already compounded with varying proportions, and leaving at the desired temperature until equilibrium was attained, which was determined by carrying out analyses for free sulphur at intervals. Finally, free and combined sulphur was determined and the free sulphur plotted against vulcanisation coefficient. It was found that at temperatures of 55°, 75°, and 95° C. the curves thus obtained were straight lines, showing that the solubility varies directly with the coefficient, but satisfactory values could not be obtained when the combined sulphur exceeded 7%, as the hard compounds did not permit of ready permeation by the free sulphur.

The effect of heating rubber films in the dark at temperatures up to 70° C. has been investigated by K. Asano,[83] who finds that, as evidenced by the solution viscosity, little change occurs in gases such as carbon dioxide, hydrogen, nitrogen, and oxygen. Light is said to produce concurrent "depolymerisation" and "polymerisation," the polymerised rubber being insoluble.[84]

AGEING.

The presence in tacky rubber of aldehydes, and particularly of lævulinic aldehyde, was noted by Gorter,[85] who found that an aqueous extract of the rubber gave the pyrrole reaction on heating with ammonium acetate.

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[81] *India Rubber World*, 1922, **66**, 494.

[82] *J. Ind. Eng. Chem.*, 1922, **14**, 319.

[83] *J.*, 1922, 301A.

[84] *Cf.* B. D. Porritt, *Rubber Age*, 1920, 445; Van Rossem, *J.*, 1915, 671.

[85] *J.*, 1915, 1104.

The subject has been taken up by G. Bruni and C. Pelizzola,[86] who have not only been able to confirm Gorter's observation regarding the presence of lævulinic aldehyde in tacky raw rubber but have also succeeded in detecting it in various samples of aged vulcanised rubber. From this it is concluded that the tackiness of raw rubber and the ageing of vulcanised rubber are, if not wholly brought about by, at any rate accompanied by similar chemical reactions.

These observations have been corroborated by F. Kaye[87] and G. S. Whitby,[88] the latter of whom identified the aldehyde by means of its pyridazinone.

Bruni has further[89] shown that artificial ageing induced by heating strips of vulcanised rubber in a closed tube at 77° C. for a period of ten days yielded a positive pyrrole test, a fact which points to the similarity of natural and artificial ageing from the chemical point of view.

The changes in mechanical properties which accompany the ageing of vulcanised rubber have been studied by W. W. Evans,[90] employing the methods described by W. C. Geer and W. W. Evans.[91] It is shown that the samples do not harden as in natural ageing, but there is a gradual reduction in the breaking load and similarly in the elongation with a given load, so that the stress-strain curves become shorter and fall lower, although not altering greatly in general form. In the case of similar mixings, the results obtained by this method are not exactly comparable with those obtained by allowing natural ageing to take place; that is to say, if it is assumed that one day of accelerated ageing is equal to six months under ordinary conditions. The opinion is expressed that a too rapid degradation is more frequently due to improper vulcanisation than to any specific effect of compounding ingredients present in the mixing.

ACCELERATORS.

The subject of accelerators still continues to attract attention, but the character of the work published tends to be more closely concerned with the mode of application in the factory than with the purely theoretical aspect of the question.

It is well known that when accelerators are used the proportion of sulphur employed in the mixing should be kept as low as possible and P. Schidrowitz and J. R. Burnand[92] have carried out experiments to determine the proportion of accelerator which must be used in order to give satisfactory vulcanisation in mixings containing 2% and 4% of sulphur. The work has now been extended to a consideration of the reverse condition by P. Schidrowitz and P. L. Bean,[93] who employed a mixing containing zinc oxide and a constant proportion of accelerator, piperidine piperidyldithiocarbamate dispersed on colloidal clay, and introduced sulphur in proportions varying from 1·07% to 4·49% calculated on the rubber. The proportion of active accelerator used was 0·5%, and it was found that approximately 2·5% of sulphur was necessary for the accelerator to exhibit full activity; below this percentage the products gave poor tensile figures.

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[86] *India Rubber J.*, 1922, **63**, 415.
[87] *Ibid.*, **63**, 535.
[88] *Ibid.*, **63**, 742.
[89] *Ibid.*, **63**, 814.
[90] *J.*, 1922, 601A.
[91] *India Rubber J.*, 1921, **61**, 1163.

A somewhat similar investigation dealing with hexamethylenetetramine is recorded by C. S. Williams,[94] working on a basis mixing of rubber 100, zinc oxide 3, to which sulphur was added in proportions varying from 1·5% to 7·0% and hexamethylenetetramine to the extent of from 0 to 1·25%. With the lowest sulphur content only fair results were obtained with 0·5% hexamine, no improvement being observed on increasing this proportion. The best results as indicated by breaking load and elongation at break were obtained by employing 3% sulphur with 1% hexamine: the ageing properties of the samples were not examined.

The relative merits of the coefficient of vulcanisation and the mechanical properties as indicated by the stress-strain curve as a means of determining the state of cure have been much debated of late years. It has been urged tha[illegible]ile the tensile characteristics may indicate clearly the value of a particular sample at the time the test is carried out, the vulcanisation coefficient is a surer index to its ageing properties. With the introduction of organic accelerators it soon became apparent that it was impossible to fix a definite standard vulcanisation coefficient applicable to all mixings, and it has been suggested by several workers that the variations observed in the coefficient of accelerated mixings of the same physical state of cure are in a measure explicable by the different times of heating necessary for vulcanisation.

N. A. Shepard and S. Krall[95] have sought to eliminate the effect of this varying heat period by selecting mixings containing different accelerators in such proportions that the time of cure of each mixing to give physically comparable products was the same. Basic mixings containing rubber (48 parts), zinc oxide (48), and sulphur (3) were selected and hexamethylenetetramine (0·5), aldehyde-ammonia

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[92] *Ann. Repts.*, 1921, **6**, 369.

[93] *J.*, 1922, 324T.

[94] *India Rubber World*, 1922, **66**, 490.

[95] *J. Ind. Eng. Chem.*, 1922, **14**, 951.

(0·75), thiocarbanilide (1·5), and *p*-nitrosodimethylaniline (0·25) added to separate batches. After heating for a period judged to be a "good commercial cure" (in this case 60 minutes at 141·7° C.) the samples were analysed by the method outlined by W. J. Kelly (p. 331) and the true combined sulphur determined. The vulcanisation coefficients were found to be in the case of hexamine 0·87, *p*-nitrosodimethylaniline 1·03, aldehyde-ammonia 0·98, and thiocarbanilide 1·38, from which it follows that even in mixings adjusted so that equivalent stress-strain relations are obtained with the same time of cure, the vulcanisation coefficient is not necessarily uniform.

The fact that the activity of certain accelerators is much enhanced by the presence of zinc oxide has been realised for some time, and in an extensive series of experiments with dithiocarbamates and similar compounds, D. F. Twiss, S. A. Brazier, and F. Thomas[96] have clearly shown the marked influence which is thus exerted.

In all cases a 90 : 10 rubber sulphur mixing was taken as the basis, and the various ingredients added in the desired proportions. When 0·25% of piperidine piperidyldithiocarbamate was present satisfactory tensile properties were obtained by curing for 180 min. at 128° C., the vulcanisation coefficient being 4·07. Addition of only 1% of zinc oxide reduced the time of cure at a lower temperature, viz., 118° C., to about 20 mins., the vulcanisation coefficient falling to 2·0. With increasing proportions of zinc oxide up to 20% the effect, judging from the figures quoted, was not so much to reduce the time of cure as to improve the maximum tensile properties of the vulcanisates. At a temperature of 128° C. the activating influence of the zinc oxide is more clearly shown. The "depolymerising" influence of this accelerator when used in conjunction with 1% of zinc oxide is clearly exhibited by the extensibility curve, as with increasing time of cure the initial reduction in extension is followed by a gradual increase. This depolymerisation is also noted in the case of other accelerators such as thiocarbanilide, tetramethylthiouram disulphide, diethylamine diethyldithiocarbamate, and zinc ethylxanthate; in the first two mentioned it is apparent only in presence of small proportions of zinc oxide, but the others appear to produce this effect even with larger proportions of oxide. The activating influence of zinc oxide is again apparent in all these cases, and it is noteworthy that even zinc salts, such as those of the alkyl dithiocarbamates, require the presence of zinc oxide to bring out the full accelerating effect. That this is not a case of surface catalysis was shown by introducing colloidal clay in place of the zinc oxide, when no such effect was produced. An interesting observation is that dithiocarbamates derived from primary amines are less active than those resulting from secondary amines, and the same is true of the thiouram disulphides prepared from these compounds. In general the authors have shown that the accelerators examined give products of initial high tensile strength and further emphasise the fact that the maximum tensile properties are obtained concurrently with a low coefficient of vulcanisation. It must, however, be remembered that the mixings employed contained a comparatively high proportion of sulphur, and that the ageing properties of the vulcanisates are not indicated.

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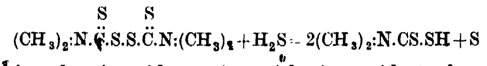
[96] *J.*, 1922, 81T.

Dithiocarbamates have been also studied by P. Schidrowitz, J. M. S. de Gouvea, and F. G. Osborne,[97] who have compared the relative activity of dimethylamine dimethyldithiocarbamate and the diethylamine analogue and have found that the dimethylamine derivative is the more active in the presence of zinc oxide, but there is little difference in activity in absence of zinc oxide. Equal weights and not equal molecular equivalents were employed, and therefore on this ground alone a more marked activity would be expected in the case of the one possessing the lower molecular weight. It would be interesting to know whether by taking molecular equivalents the difference would still persist. It is worthy of note that both the compounds are active in the absence of zinc oxide, thus confirming the work of P. L. Bean,[98] who disputed the correctness of the statements by J. B. Tuttle,[99] to the effect that under these circumstances vulcanisation is actually retarded.

Continuing their studies on the reactions of accelerators during vulcanisation,[100] C. W. Bedford and L. B. Sebrell[101] find that tetramethylthiuram disulphide, if present to the extent of 5%, will vulcanise rubber equally well in presence or absence of zinc oxide. The samples containing zinc oxide show higher tensile properties, but the vulcanisation coefficient is lower, and a considerable proportion of zinc sulphide is formed. This thiouram disulphide will not vulcanise rubber cements containing sulphur in the cold, either when used with or without zinc oxide ; in presence of hydrogen sulphide, however, vulcanisation takes place, but only in the cement containing zinc oxide. This is explained by the formation of the dithiocarbamic acid, with liberation of sulphur, which is available for vulcanisation :—



$$(CH_3)_2{:}N.\overset{S}{\ddot{C}}.S.S.\overset{S}{\ddot{C}}.N{:}(CH_3)_2 + H_2S = 2(CH_3)_2{:}N.CS.SH + S$$

the dithiocarbamic acid reacting with zinc oxide to form the zinc salt.

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[97] *India Rubber J.*, 1922, **64**, 75 ; *J.*, 1922, 601A.

[98] *Ibid.*, 1922, **63**, 354 ; *J.*, 1922, 261A.

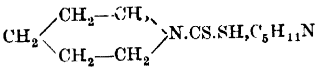
[99] *J. Ind. Eng. Chem.*, 1921, **13**, 521 ; *J.*, 1921, 709A.

[100] *Ann. Repts.*, 1921, **6**, 365.

[101] *J. Ind. Eng. Chem.*, 1922, **14**, 25 ; *J.*, 1922, 262A.

When employed in hot vulcanisation thiouram disulphides form alkylated ammonium polysulphides and trithiocarbamates, while in presence of zinc oxide salts of dithiocarbamates are formed in addition. Dithiocarbamates will bring about vulcanisation of cements at low temperatures but only in presence of zinc oxide, and in curing at high temperatures the zinc salts do not react readily with sulphur, except through hydrogen sulphide produced by reaction with the rubber resins. Thiocarbanilide is said to function as a mercaptan,[102] and the zinc mercaptide formed reacts with sulphur giving a polysulphide, which furnishes the sulphur necessary for vulcanisation. In this case there will be no metallic sulphide formed, as is postulated in the theory of Bruni and Romani, who assume that the mercaptide is converted into a mercaptobenzothiazole disulphide with simultaneous formation of zinc sulphide. The activity of guanidines is also explained by Bedford and Sebrell, on the basis of the polysulphide theory, but discussion of the nitroso compounds is reserved for a future occasion.

The writer would like to call attention here to the nomenclature generally adopted in describing the reaction product of piperidine and carbon disulphide.



to which the name piperidine piperidyldithiocarbamate is given, and this has been used for convenience in this report. Piperidyldithiocarbamic acid, however, would be represented by the formula $C_5H_{10}N.NH.CSSH$ in which one of the hydrogen atoms of dithiocarbamic acid NH_2CSSH is replaced by the piperidyl group $C_5H_{10}N$-. In the compound under consideration the two hydrogen atoms are replaced by the divalent pentamethylene group and the correct designation would be pentamethylene dithiocarbamate, a name which has occasionally been used.[103] If it is desired to retain the piperidine group in the name the designation becomes more difficult, but either piperidine-1-carbodithionic acid or piperidylcarbodithionic acid would be equally correct.

Several papers reviewing the subject of accelerators have appeared during the year,[104] and as a matter of historical interest it has been stated that organic accelerators were first used in America by G. Oenslager in 1906, thiocarbanilide being introduced in 1907.[105]

[102] *Cf.* G. Bruni and E. Romani, *India Rubber J.*, 1921, **62**, 63; *J.*, 1921, 553A.

[103] G. Bruni, *J.*, 1921, 400A; Murril, *Le Caoutchouc et la Gutta Percha*, 1922, 11, 262.

[104] J. L. Rosenbaum, *India Rubber J.*, 1922, **63**, 225; C. W. Bedford, *J. Ind. Eng. Chem.*, 1922, **14**, 856; L. E. Weber, *India Rubber J.*, 1922, **63**, 793.

[105] W. C. Geer, *J. Ind. Eng. Chem.*, 1922, **14**, 373.

Although one gathers that the number in actual commercial use is very limited,[106] accelerators mentioned in technical literature are exceedingly numerous and a proposal has been made to issue an index and complete bibliography dealing with the subject, arrangements for which are in the hands of C. W. Bedford.[107]

TESTING.

The machine usually employed in Europe for determining the tensile properties of vulcanised rubber is of the Schopper type, which, operating on a ring-shaped test piece, autographically records load applied and elongation. For those who do not possess such a machine, or for other reasons prefer to use a dumb-bell shaped test piece, W. W. Vogt[108] has devised a new type of stress-strain curve. This is obtained by plotting the load necessary to produce given elongations at increasing times of cure against times of cure expressed in hours or minutes. Elongations increasing by 100% are chosen and for each elongation a separate curve is obtained.

Comparison of various mixings may then be made by a visual examination of the curves thus obtained, and, if required, the normal stress-strain curve for any of the cures can be constructed from the data and recorded on the same graph, the elongation being plotted on the same axis as the time of cure. The reverse method, wherein the elongations at a given load are plotted against times of cure, has been frequently employed by D. F. Twiss and others.

In view of the divergent methods of graphically recording various mechanical properties of rubber, a plea for standardisation has been entered by W. B. Wiegand,[109] who urges that the whole of the mechanical characteristics be set forth on a single sheet of squared paper divided into six sections. On the left hand side of the chart breaking load, elongation at break, and sub-permanent set after rupture, are to be plotted as ordinates against time of cure as abscissæ. On the right hand side energy of resilience and tensile product are plotted against time of cure in the lower section, and in the upper section the stress-strain curve, contrary to the usual practice, is shown with elongation as abscissæ and loads as ordinates. The stress-strain curve is thus brought into conformity with modern engineering practice in recording data obtained with constructional materials, and in effect the result is the same as would be obtained by turning the ordinary Schopper curve through an angle of 90°.

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[106] L. E. Weber, *loc. cit.*

[107] *India Rubber World*, 1922, **66**, 561.

[108] *Ibid.*, 1922, **65**, 421.

[109] *India Rubber J.*, 1922, **64**, 889.

A. H. Nuckolls[110] has drawn attention to the effect of temperature at which mechanical tests are carried out on the results obtained, the breaking load for instance, decreasing markedly with increasing temperature, a fact to which attention has been frequently directed.

W. W. Evans[111] has devised a machine for obtaining stress-strain data, and particularly hysteresis loops at low elongations, these conditions being in conformity with actual usage. It is suggested that much of the disparity of stress-strain data is due to non-standardised conditions of applying the load. In the machine described, which is of the balance type, the load is applied and released at a uniform rate per unit area of cross-section, and this is accomplished by using a bucket which can be moved either towards or away from the fulcrum, according to the cross-sectional area of the test piece.

It is well known that certain rubber mixings are more liable to tear apart than others once a cut has been made. Attempts have now been made to express this "tearability" quantitatively by E. C. Zimmerman,[112] by J. B. Tuttle,[113] and by B. B. Evans.[114] From the results of the last-named it would appear that in compounds containing equal volumes of pigment, refined china clay causes tearing more readily than does magnesium carbonate, while zinc oxide gives products which can scarcely be torn. Overcuring increases tearability in a normal mixing, but if an accelerator is introduced the reverse is the case, overcuring giving better results than under- or correctly-cured samples, the general effect of adding accelerator being to increase resistance to tearing. The method of curing also appears to have some influence on the results obtained, and this may, in a measure, be due to the manner in which the samples are built up. The methods outlined by these workers constitute a new departure in the mechanical testing of rubber, and while it is at present impossible to draw any general conclusions, further developments will be awaited with interest.

Comparisons of the permanent set of vulcanised rubber samples under various conditions have been made by F. W. G. King and A. G. Cogswell,[115] who have determined the effect of varying the extension, time of extension, and time of recovery, and have also studied the effect on the set of extension under constant load. They conclude that application of stress for 20 minutes and a recovery period of one hour should suffice for routine testing, although, if greater accuracy is desired 3–5 hrs. should be allowed; the method of using constant extension rather than constant load is favoured, and high extensions are said to give more uniform results than low extensions.

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[110] *India Rubber World*, 1922, **67**, 79.

[111] *Ibid.*, 1921, **65**, 192.

[112] *India Rubber J.*, 1922, **64**, 475.

[113] *India Rubber World*, 1922, **67**, 150.

[114] *India Rubber J.*, 1922, **64**, 815.

[115] *India Rubber J.*, 1922, **63**, 30; *J.*, 1922, 110A.

In connexion with the use of rubber for shock absorbers, especially for aeroplanes, a communication by H. P. Gurney and C. H. Taverner[116] possesses many points of interest. The energy-absorbing capacity of mixings made up with plantation and Para rubber, with and without additional ingredients, was determined, and curves are given showing hysteresis in successive cycles of extension and retraction.

Articles dealing with dielectric tests on insulating materials have been published by N. A. Allen,[117] who describes a guard ring for use when testing at the edges of a sheet, W. S. Flight,[118] and the British Electrical and Allied Industries Research Association,[119] who have issued particulars of a comprehensive series of tests for insulating materials including vulcanised rubber.

ANALYSIS.

The proportion of rubber hydrocarbon present in vulcanised samples is generally arrived at by a difference method, the percentage of other known constituents being determined directly, and several attempts have, from time to time, been made to elaborate a scheme for the direct determination of rubber. The formation of caoutchouc tetrabromide has served as the basis of several methods, and that of W. K. Lewis and W. K. McAdam,[120] in which the hydrogen bromide formed by substitution is determined by allowing it to react with iodate and titrating the iodine liberated, appeared promising as it overcame one of the chief objections to the methods then available. The method has been investigated by H. L. Fisher, H. Gray, and R. Merling,[121] who have introduced several modifications, notably the drying of the tetrachlorethane used for bringing about "solution" of the vulcanised rubber, and increasing the proportion of potassium iodide so as to react with the whole of the excess bromine. These workers, however, failed to obtain satisfactory results, an error of more than 24% being recorded in the case of a pure rubber sample, and they therefore conclude that further elaboration is necessary before the method can be used with any degree of confidence.

For the determination of the bromine content of caoutchouc tetrabromide, F. Utz[122] recommends treatment with a solution of silver nitrate and potassium bichromate in concentrated sulphuric

[116] *J. Ind. Eng. Chem.*, 1922, **14**, 134 ; *J.*, 1922, 183A.
[117] *India Rubber J.*, 1922, **63**, 61.
[118] *Elec. Rev.*, 1922, **90**, 39, 76.
[119] *India Rubber J.*, 1922, **64**, 29.
[120] *Ann. Repts.*, 1920, **5**, 349.
[121] *J. Ind. Eng. Chem.*, 1921, **13**, 1031 ; *J.*, 1922, 110A.
[122] *J.*, 1922, 383A; see also *J.*, 1912, 329.

acid, warming gradually, and absorbing the liberated bromine in a mixture of equal volumes of 15% sodium hydroxide and saturated sodium sulphite solution. The bromine content of the absorption liquid is estimated after acidifying with nitric acid.

J. Lagerqvist[123] states that the drying of acetone extracts obtained in the analysis of rubber goods should be carried out at 50° C. under reduced pressure, as drying at 100°–105° C. at ordinary pressure yields lower, and more variable, results.

The various forms in which sulphur may be present in vulcanised rubber mixings have been exhaustively studied by W. J. Kelly,[124] who has extended his earlier work,[125] which dealt only with " pure " mixings, to those containing various compounding ingredients, including zinc oxide, litharge, glue, with and without organic accelerators. The sulphur may be present in the acetone-soluble portion, either as true free sulphur, or as sulphur in combination with resins, proteins, and accelerators. The acetone-insoluble portion may contain sulphur combined with the rubber, together with resins, protein, and accelerators. Apart from cases where sulphates such as barytes have been added, sulphur may also be present in metallic sulphides either previously added or formed during vulcanisation, and H. P. Stevens[126] has already described a method of analysis for use in such cases.

In the examination of the acetone-soluble portion Kelly performs two extractions, in the one case determining the total free sulphur, and in the other the " true free " sulphur, *i.e.*, that which remains after washing the extract with alcohol previously saturated with sulphur, which dissolves only the organically combined portion.

In the acetone-insoluble portion of the sample, the determinations consist of : (1) total sulphur ; (2) sulphur soluble in alcoholic potash, which includes that portion which is in combination with resins etc. ; (3) metallic sulphides determined according to Stevens' method; (4) sulphur combined with accelerators etc., dissolved in the ether-hydrochloric acid reagent and remaining after hydrogen sulphide has been evolved ; (5) sulphur combined with rubber.

Results of analyses carried out in this manner are quoted, but it can hardly be said that the figures justify the adoption of the somewhat elaborate scheme for ordinary analytical purposes. In cases where research is being undertaken on the reactions involved when accelerators are employed, the methods outlined should prove useful, as it must be confessed that, with a few notable exceptions, little positive evidence such as a method of this description would furnish has been adduced in support of theories. Looking at the

[123] *J.*, 1922, 183A.
[124] *J. Ind. Eng Chem.*, 1922, **14**, 196 ; *J.*, 1922, 301A.
[125] *J.*, 1920, 725A.
[126] *J.*, 1915, 724.

figures quoted for sulphide sulphur, it will be seen that in a zinc oxide mixing the presence of thiocarbanilide has not materially affected the proportion formed during vulcanisation, as would be expected[127] under these circumstances.

Dealing with the determination of combined sulphur in comparatively pure mixings, J. W. W. Dyer and A. R. Watson [128] advocate the use of nitric acid followed by potassium permanganate to bring about oxidation of the sulphur, as previously described by A. R. Pearson.[129] For the determination of free sulphur the acetone solution is oxidised directly with potassium permanganate, but it is likely that this would be effective only when the sulphur extracted remains dissolved in the acetone and not, as so frequently happens, when it has begun to crystallise out. S. G. Byam [130] recommends the use of the Parr sulphur bomb for rapidly determining free sulphur, the barium sulphate, after precipitation, being weighed directly or estimated by means of a nephelometer.

A method described by I. R. H. ter Meulen [131] consists in passing hydrogen over the heated sample and then over heated platinised asbestos so as to convert any sulphur into hydrogen sulphide, which can be determined iodometrically. While this may be suitable in some cases, there will doubtless be a danger of poisoning of the catalyst in samples containing antimony or mercury.

Methods of analysis of guttapercha are briefly outlined by V. A. Stock,[132] and among recent publications dealing with rubber analysis may be mentioned the Fourth Edition of U.S. Bureau of Standards Circular No. 38, which also deals with physical tests, and the Methods of Analysis tentatively recommended by the American Chemical Society (Rubber Division).[133]

MISCELLANEOUS.

Considering that almost without exception the heat necessary for vulcanisation is afforded by means of a steam supply, although P. Schidrowitz[134] has visualised its substitution by hot water, the proposal to employ a high-boiling liquid such as aniline [135] is not without interest, especially as such methods of heat transmission are now attracting attention.[136] A novel method of making use of the property possessed by eutectic alloys of maintaining a constant temperature during solidification is proposed in a patent[137] for employing an alloy of tin (25 pts.), lead (16 pts.), and cadmium (9 pts.) which maintains a temperature of 145° C. while the solid and liquid phases exist together. Such alloys would be suitable for use with portable vulcanisers, for carrying out casual repairs.

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[127] *Ann. Repts.*, 1921, **6**, 368.

[128] *J.*, 1922, 251T.

[129] *Ann. Repts.*, 1920, **5**, 349.

[130] *India Rubber World*, 1922, **66**, 678.

[131] *J.*, 1922, 235A.

[132] *India Rubber World*, 1922, **66**, 613.

[133] *J. Ind. Eng. Chem.*, 1922, **14**, 560.

[134] *India Rubber J.*, 1922, **63**, 68.

[135] R. Wheatley and Victoria Rubber Co., E.P., 181,802 ; *J.*, 1922, 549A.

[136] *Ann. Repts.*, 1921, **6**, 6.

A modification of the gas absorption process for producing cellular rubber [138] consists in incorporating finely-divided charcoal with the rubber mixing, thereby increasing the absorptive capacity of the mass, and allowing the employment of lower atmospheric pressures.[139]

Brief reference may be made to the suggested use of rubber in making transparent substitutes for glass, in one case the rubber being mixed with celluloid in a common solvent, cyclohexanol, from which a rubber-celluloid film is obtained,[140] or the rubber, supported, if necessary, on a gauze structure, may be employed alone and cured by the Peachey process.[141]

[137] B. Lambert, E.P. 183,590 ; *J.*, 1922, 772A.
[138] C. L. Marshall, E.P. 162,176 ; *J.*, 1921, 439A.
[139] K. H. Fulton, E.P. 185,477 ; *J.*, 1922, 868A.
[140] R. Ditmar, *J.*, 1921, 709A.
[141] *India Rubber World*, 1922, 66, 538.

LEATHER AND GLUE.

By D. Woodroffe, M.Sc., A.I.C.

Head of Leather Department, Northampton Technical School.

The leather trade has experienced a most uncomfortable period during the past year. The heavy leather section, which is the most important, has had the most prosperous time, if anybody has been prosperous. As mentioned in last year's report,[1] hides slumped to an unprecedentedly low figure in 1921, but tanners were holding off buying them. They were enabled to dispose of those hides which were put into work at a profitable figure, but the volume of business has been small because of the restricted purchases of raw material. Raw material has become firmer in price and with the upward tendency, tanners have endeavoured to obtain higher figures for their leather.

The situation has been materially influenced by conditions in America, where hides are 50% dearer than here. It is difficult to understand the rise in price, and it has been suggested that the packing firms hold big stocks of tanned leather, which they find difficulty in disposing of, and to enable them to find a ready market they are purposely inflating the price of the raw material. When the finished leather has risen in price, these stocks will be unloaded on the market at a profitable figure. This suggestion is very possible but the secret of the trouble lies deeper than that. It seems hardly feasible that there can be much leather in the States, otherwise British tanners would not be finding such a ready market for their productions in that country.

Cattle breeding and rearing has proved anything but profitable during the past eighteen months. Prices are still falling, and have been falling during the whole of 1922. Cattle purchased in 1921 at prices ranging from £50 to £70 each, have only realised from £17 to £45, and farmers and stockbreeders have had no inducement to stock large herds; on the other hand, there has been every reason for drastic reductions in the numbers until such time as prices are stabilised and there is no longer any grave risk of seeing capital melt away. Combined with these facts is the smaller number of animals which have been slaughtered during the year.

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[1] *Ann. Repts.*, 1921, **6**, 379.

Unemployment and lower wages have seriously diminished the purchasing power of the community, the "kill" is much less than normal,[2] and hides are comparatively scarce. America has no leather to spare for export to-day, as the demand there is sufficiently steady to utilise all their productions. The British sole leather market is almost entirely dependent upon home supplies. In ordinary circumstances this would have been the tanner's opportunity, but all attempts to obtain advances in the home markets have proved fruitless. Tanners have sought to obtain advances of 1d. and 2d. per lb., but their demands have met with an unreserved refusal. Leather factors and boot manufacturers alike are running down their stocks in the hope that the low prices will be re-established.

Tanners have resorted to the old method of reducing the quantity of hides put into the pits in the hope that raw hides will become cheaper, but it is difficult to see how this can be achieved when American hides are realising 1s. 6d. per lb., against English hides at 10d. The situation is very complex, and it seems probable that sole leather must increase in price. Trade has been very fair on the whole, but boot manufacturers are very hard-pressed to produce boots at a reasonable price and they are on the look-out for cheap leather.

There have not been many technical developments in the tanning of sole leather, except in minor details. The use of synthetic tannins is becoming more general and seems likely to involve chemists in a difficult position since the combined sulphuric acid in the synthetic tannins is reported as free mineral acid, according to the Procter-Searle method of the mineral acid determination. A further complication arises from the increasing application of sulphonated oils to the finished leather. It is surprising how much oil is found in some tannages, and the question of a limit has been considered again by one Research Association. The standards suggested were as follows : Ash, 2% ; water-soluble matter, 22% ; fat, 5%, and free mineral acid, 0·5%.

The light leather and dressing leather section of the trade has experienced a very trying time during 1922. The Government has had large stocks of East Indian tanned kips in its possession which have been left over from purchases made during the war. The stock in hand two years ago was sufficient to cover the whole of the requirements of the home trade for a period of twelve months. The existence of such stocks has greatly depressed the markets, and it was only in November that the whole of these stocks was cleared, with the result that the kip trade has revived and prices have shown buoyancy. Direct imported kips are commanding more money, and there has been an improved turnover.

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[2] *Yorkshire Post*, Oct. 26, 1922.

Leather dressers and dyers of tanned leathers have been fairly busy during the year at keenly competitive prices. Some manufacturers have declined to compete for business and they have been left stranded with a few crumbs of trade. There appears to be a keen demand for technically trained dyers, managers, and foremen. Some firms are quite unable to compete with the foreigner in dyeing and finishing. English dyes are much superior to pre-war production, but they cannot yet be compared with the pre-war German dyes on leather.

The most serious feature of the past year has been the terrible plight of the chrome tanning section. Many firms specialising in chrome productions have been compelled to close down, owing to the keen foreign competition. The first blow was the release of large quantities of American calf and sides at slump prices. This was followed by a corresponding fall in the prices quoted for French and German productions, which was rendered possible by the anomalous rate of exchange. It has been impossible for British tanners to compete with the prices quoted, and many are waiting until conditions improve before venturing again on box and willow manufacture. The only profitable section of chrome calf tanning has been the manufacture of suede and white calf. Firms who were equipped for this work have been able to continue both the production of grain and suede calf. The outlook is very black. Raw calf are scarce and consequently dear ; the demand for suedes is uncertain and speculative. A large amount of capital has been sunk and much lost in attempts to capture the foreign trade. Five or six chrome tanneries, which were commenced during the war, in the Midlands have either closed down, or are working out a mere existence. In two cases the standard of production was remarkably high, and the box-calf produced at one tannery compared favourably with continental productions, whilst the glazed kid turned out by the other factory was superior to much of the American glazed kid. Only well-established chrome tanneries appear to have been able to weather the last two years, and fortunately there are a few who can compete with the foreigner and beat him in the home markets.

The gloving trade has experienced a very successful year as regards the volume of work. The demand for fine suede leathers in high-class shoes has taxed the utmost capacities of the home trade, and some very fine leather has been turned out by English glove dressers in all the different shades decreed by fashion. There has not been much extension ; in one instance it was proposed to erect a new works, but the local authorities objected to any addition to the number of works occupied in this most "objectionable" trade. It seems very unfortunate that so much prejudice still exists. The leather trade is one of the healthiest, and the old disgusting and nauseous processes are speedily being replaced by more scientific methods in which pure, sweet, clean materials are employed, and odour and putrefaction are obviated. The change which has been wrought in the bating process is almost miraculous. In 1914 only two or three British firms were using scientifically prepared bating materials, and most tanners relied on dog and bird excrements for their bating process. Most tanners claimed that it was impossible efficiently to replace the old-fashioned materials, and the arguments of the chemist were dismissed with contempt. To-day there are only two or three large firms who are not using the scientifically prepared bating material regularly and exclusively for their bating process. The change has come about very quietly, and largely owing to the dogged perseverance of certain workers, but it is a triumph for applied chemistry.

There have been several improvements in leather machinery during the past twelve months. A new shaving machine has been introduced from Germany, by means of which shaving has been reduced to a semi-skilled operation. The machine can be adjusted for any desired substance of leather, and in one stroke of the machine the substance of stouter skins is automatically reduced to this substance. A kip side can be shaved in three strokes, thus very much reducing the time occupied in shaving stout chrome skins at present. The machine has been introduced into several English leather works, and has proved a great success.

New and improved machines are being built for striking out and samming, which facilitate the manufacture of leathers with a better appearance. The grain is well got out, and the wrinkles on bull hides and skins can be removed. There has been an increase in the number of scientific drying plants in operation, and leather manufacturers are realising more than ever the need for efficiency in the drying shed. An Act was passed in 1919 relating to instruments for measuring leather by superficial area. The regulations made under that Act did not become operative until July 1st, 1921. The Act at present only applies to leather-measuring machines of patterns approved by the Board of Trade. The only machine approved at present is a new pin-wheel type of machine, of which there are only three or four in existence. It will probably not be long before the Act is amended to enforce the use of approved machines only. Approved machines are subject to inspection, with a view to testing, verification, and stamping.

Encouraging reports have been issued by the different educational institutions. Leeds University Leather Industries Department has had a most successful session, and some brilliant students have just completed their course there. The Leathersellers' Technical College has been very busy, and the students have scored many successes in the external examinations. Efforts are being made to train youths at the Northampton Technical School for positions where technical knowledge is indispensable, and the leather department is full of students. The educational aspect of the leather trade is extremely important, because there is such an urgent need for the present knowledge to be disseminated throughout the trade. There is a scarcity of young men who can fulfil the obligations of executive positions requiring technical knowledge. Chemists do not realise the need for themselves applying their knowledge in works' processes, and they expect non-scientific foremen and managers to realise their point of view. The various research associations are doing a most valuable work in educating the tanners and manufacturers, which is generally forgotten when the value of their work is being assessed.

Several valuable books have been published during the year, the most important of which has been the second edition of Procter's "Principles of Leather Manufacture."[3] This book, first published in 1903, has long been considered to be the standard work on leather manufacture. It has proved a stimulus to thought, as well as a guide to methods. The latest information on proteins and tannins has been included and there are valuable chapters on colloids and physical chemistry. F. G. A. Enna[4] has translated G. Grasser's book on "Synthetic tannins," Dr. A. Rogers[5] has modernised L. A. Flemming's "Practical Tanning," and added some valuable information on unusual tanning processes, pigment finishes, and patent leather. J. Jettmar[6] has written an up-to-date treatise on vegetable tanning materials and extracts. Each material is described in turn, and complete analyses of different samples are cited. An excellent introduction to the chemistry of the tannins is also included. F. Kopecky has written a small brochure on "Theory and Practice." M. C. Lamb has outlined the manufacture of chrome leather in an American journal,[7] and is about to publish a book on the same subject.

The Leathersellers' Company arranged another series of lectures in the last month of the year. The first two were delivered by Dr. R. H. Pickard,[8] director of the Leather Manufacturers' Research Association, and he outlined some of the problems at present under consideration by the staff of the Leather Trades Research Association. He stated that the Association had solved the problem of spueing on chrome leathers. One member of his staff has prepared a chromium compound by means of which pelt can be one-bath chrome tanned and which causes a spue under certain conditions, which can be controlled. The main portion of the lecture was devoted to an account of the microscopical investigations which had been carried out on goatskins, sheepskins, and ox-hides in the raw state, and after treatment with acids, alkalis, sodium sulphide, ammonia, lime, and after bating. Some excellent sections had been prepared and photomicrographs made from them. Lantern slides of these were employed to illustrate the lectures, and they revealed evidence of a large amount of careful painstaking research.

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[3] *J.*, 1922, 321R.
[4] *J.*, 1922, 141R.
[5] *J.*, 1922, 488R.
[6] *Leather Trades Rev.*, 1922, 378.
[7] *Shoe and Leather Reporter*, 1922
[8] *Leather Trades Rev.*, 1922.

A lecture on the Warble fly was delivered by Prof. G. H. Carpenter[9] on the following day, and preventive measures explained for obviating serious damage to the hide. The lecturer described the two species of warble fly. The *bovis* variety is the most prevalent in England and Ireland. The fly lays its eggs at the lower end of the hairs on the animal's hocks, the eggs hatch and the young maggots bore through the skin and migrate to the gullet from whence they travel to the back. When ripe, the maggots bore through the most valuable portion of the hide and fall to the ground. The most successful remedial wash consists of an infusion of tobacco waste and some alkali.

The leather trade has sustained a very serious loss through the death of three of the leading continental experts, W. Eitner, W. Fahrion, and J. Jettmar. Eitner[10] was the founder of *Der Gerber*, which rightly claims that he and his assistants have performed an enormous amount of work during the last forty years. He has carried out fundamental investigations in tanning chemistry, and has assembled and published an extraordinarily large amount of practical knowledge. He was the author of the three-bath chrome tanning process, and has inspired many of the younger experts in chrome tanning.

W. Fahrion[11] died on February 21st. He was one of the greatest oil chemists of his day, and was the leading authority on oils and fats connected with the leather trade. He has made valuable contributions to the theory of leather formation and was one of the first to propound a chemical theory of tannage. He manifested a keen interest not only in theoretical aspects, but also in the practical side of the leather industry, and took out several patents on aldehyde and chamois tanning. He instituted the water-resistance test for leather which is still known by his name.

J Jettmar[12] succeeded to W. Eitner as editor of *Der Gerber* when the latter retired in 1910. He has been one of the most prolific contributors to the technical knowledge of the trade and a most valuable contribution[13] from his pen appeared in the early months of the year.

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[9] *Ibid.*, 1922, 1020.
[10] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 3.
[11] *Ibid.*, 1922, **17**, 533.
[12] *Leather World*, 1922, 1076.
[13] *Cf.*[6]

SOAKING AND LIMING, ETC.

More and more emphasis is being placed on the importance of the time which elapses between the slaughtering and flaying of the animal and the curing of the hide or skin, or the period before the hide is worked up by the tanner. Hitherto no systematic study has been made of the experimental evidence afforded by the curing process, but G. D. McLaughlin and E. R. Theis [14] have remedied this defect. Curing with salt is a movement of salt into the hide, and water out. There are two processes of salt-curing, either with salt alone or salt solutions, the latter being known as brining. When hides are salted or immersed in a 25% solution of brine the hide loses water. Of the three chief layers of the hide the adipose tissue is most dehydrated. The salt is adsorbed by the hide and the water is removed from the hide during the process, and the greater the dehydration, the greater the amount of salt adsorbed. There is no advantage gained by salting both sides of the hide, because the epidermis does not absorb the brine very readily. "The epidermis is primarily an organ of secretion and not of absorption." The crux of the problem of curing rests in the period which elapses between killing and salting. If the salting is delayed from one to six hours, the rate of diffusion of the salt into the hide is greatly reduced. If the hide is allowed to stand for varying periods of time before being salted, the salt content, after curing a hide containing blood, is lower than that of a hide from which the blood has been removed. The longer the delay the greater is the difference between the two. The diffusion of the salt is hindered by the presence and condition of the blood, by post-mortem changes, and by the composition of the salt. Hides should be salted as soon as possible after they have been flayed. Before salting, however, they should be properly washed and brined to remove the blood and its effects, to secure a maximum absorption of salt in a minimum of time, to eliminate salt and iron stains, and to minimise the effect of post-mortem changes which were shown [15] to exercise such a serious influence on the swelling power of the pelt.

The same authors have made a practical study [16] of hide curing. They conclude that when heavy hides are properly washed and brined they produce more leather when tanned than if they had not been brined. Not only is more leather produced but it is thicker and firmer, and shows a minimum of salt and iron stains. Brined stock, however, requires special beam-house treatment. Inefficient washing or brining may be harmful rather than beneficial. The hides should be washed in running water immediately after flaying, and then brined for twenty-four hours in a 25% sodium chloride solution, drained for a few minutes, and salted down with new salt. The brined stock should be given a "sharp" liming to ensure the best results. This is in accordance with the practical experience of many tanners who have found that salted skins[17] require very much sharper limes than fresh or dried stock.

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[14] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 376; *J.*, 1922, 773A.

[15] *Ann. Repts.*, 1921, **6**, 384.

[16] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 399; *J.*, 1922, 773A.

G. D. McLaughlin and G. E. Rockwell[18] have shown that the hide contains many kinds of bacteria which exert varying effects upon it. Twenty-four different varieties were isolated from thirty short-haired hides, and their individual properties as regards suitability of different media for growth were ascertained. Experiments on hide pieces previously soaked for 72 hrs. in water, dextrose, and blood respectively before liming, have shown that the presence of blood in the soak liquor increases the number of gelatin-liquefying organisms present and results in a considerable loss in weight to the pelt. Dextrose appears to inhibit the action of gelatin-liquefying organisms and the addition of 3% of dextrose to those liquors in which there is a possibility of blood being present from the hides, checks the growth of gelatin-liquefying organisms. The presence of soluble proteins, a slightly alkaline medium, a warm temperature, the presence of oxygen and small traces of carbon dioxide were found to favour bacterial decomposition of the hide, whilst the absence of proteolytic bacteria, acidity, the presence of fermentable carbohydrates, a large excess of carbon dioxide, the absence of oxygen, and a low temperature tended to prevent it.

B. S. Levine[19] records some experiments to find a method of soaking hides which would result in a minimum loss of hide substance, and which would, if possible, eliminate the prolonged process of unhairing, thus saving both time and chemicals. It has been shown that if hides are soaked in water which has been freed from air, the hair is loosened in a shorter period, and the number of bacteria per c.c. is less than under other conditions. If air is periodically bubbled through the liquid, it becomes thick and difficult to filter, whilst the liquor left after unhairing in an atmosphere of carbon dioxide is clear and easily filtered. The experiments confirm the Walker-Bolton patents,[20] in which soaking and hair-loosening are effected without the use of the customary liming agents.

Reference was made last year[21] to the increasing use of lime liquors of a definite percentage or barkometer strength. There is additional evidence this year of such a gradual change in procedure. O. Richter[22] proposes to unhair skins by placing them in closed chambers containing a definite amount of ammonia per cubic metre at 37°–45° C. T. B. Carmichael and W. H. Ockleston[23] have patented the treatment of hides first with a 0·5% solution of sodium sulphide, and then with a 0·5% solution of caustic soda. The hides may be either suspended or drummed in these liquors. Other patents for the unhairing of hides and skins include immersion in liquid air,[24] the use of dextrin, talc, essential oils, "nerolin," and maize starch powder in paints,[25] and degreasing prior to depilation and protection of the flesh side against penetration.[26] W. Rautenstrauch[27] has made an addition to his previous patent[28] in suggesting that liming liquors should be enriched with hide substance or similar albuminous matter to prevent loss of hide substance during the unhairing process.

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[17] *Leather World*, 1922, 375.

[18] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 325 ; *J.*, 1922, 640A

[19] *Ibid.*, 1922, **17**, 417; *J.*, 1922, 827A.

[20] *Ann. Repts.*, 1921, **6**, 384.

[21] *Ibid.*, 1921, **6**, 387.

[22] E.P. 175,214 ; *J.*, 1922, 304A.

Deliming and bating have been the subjects of much activity and painstaking research during the past twelve months. A few patents have been granted; one to W. Savage[29] for deliming with fuller's earth or zeolites, another to C. H. Boehringer Sohn[30] for the use of pure or crude saponified bile acids or their salts in combination with other bating materials not containing bacteria or enzymes, for bating purposes. O. Röhm[31] suggests the use of a solution of caustic alkali, alkaline-earth, or ammonia, which contains a salt of one of them, for treating hides. A neutralising agent is added, and pancreatic enzymes for bating purposes. The mixture forms a combined depilatory and bating material for hides and skins.

The staff of the British Leather Manufacturers' Research Association has entered very fully into the changes which take place in the skin during the soaking, liming, deliming, and bating processes. In the lectures[32] delivered in the last month of the year, the Director described the result of their researches. Lantern slides prepared from photomicrographs showed the structure of hides and skins in the fresh, wet-salted, dry-salted, and dried conditions. It was evident from the slides that drying and dry-salting cause the hair bulbs to curl under and this displacement was still apparent when the dry or dry-salted skins were soaked back. This would probably account for the difficulty experienced in loosening the hair on dried skins. The salting of skins, whether dry-salted or wet-salted, separates the fibres, and this is apparent both in sections of the cured skins and also sections of the skins after soaking. When salted skins are soaked back, they are thicker than similar dried or fresh skins. This is, no doubt, due to the action of the salt in having separated the fibres. Leather tanned from fresh, dried, and salted hides shows the same differences in structure. The leather from salted hides is thicker than that from dried and fresh hides, and photomicrographs of the section reveal a better separation of the fibres in the leather from salted hides.

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[23] E.P. 173,788; *J.*, 1922, 225A.

[24] E.P. 163,294; *J.*, 1922, 560A.

[25] G.P. 348,413; *J.*, 1922, 677A.

[26] E.P. 182,240; *J.*, 1922, 641A.

[27] E.P. 160,435; *J.*, 1922, 69A.

[28] *Ann. Repts.*, 1921, **6**, 386.

[29] U.S.P. 1,382,124; *J.*, 1922, 511A.

[30] G.P. 351,015; *J.*, 1922, 721A.

[31] E.P. 156,079; *J.*, 1922, 225A.

[32] *Leather Trades Rev.*, 1922, 1022.

Dr. Pickard described the effect of various chemicals on single hide and skin fibres, and also on the whole skin and hide as revealed by the microscope. The effect on the whole skin is different to that on the individual fibre because of the skin structure. Acids and alkalis caused hide and skin fibres to become distended, and also very much thicker. The action on skins was determined by treating the skin with the particular reagent, then teazing out the fibres at the edge of the skin and examining these. Slides were produced to show the effects. Caustic soda produced intense plumping of the fibres. Dr. Pickard distinguishes between "swelling" and "plumping" by describing "swelling" as the separation of the fibres and "plumping" as the absorption of water by the individual fibres with a consequent increase in thickness of such fibres. Caustic soda plumps the fibres in the skin, acids cause plumping also, ammonia merely swells the fibres, *i.e.*, separates them, whilst lime plumps and swells. It was shown that every process is reversible, and various combinations of acid action after alkali action and *vice versa*, gave the results which would have been expected from a consideration of the individual effects of the particular acid and alkali.

The difference in the action of reagents on the skin and on the individual fibres was illustrated by a magnificent photomicrograph of the bands encircling the bundles of fibres, also showing smaller bands encircling the fibrils in the individual fibres. One slide illustrated the stress or tension which existed in the bundle, and which the band controlled. As soon as the fibre bundles were cut they spread out. Bacteria in lime liquors are very short-lived and contrary to general opinion, bacteriological action could not influence the process in the liquor. Figures were quoted of a limeyard, where fresh batches of skins passed through the same lime liquor every twenty-four hours. At the end of the first hour the number of bacteria per c.c. was considerable, but this number rapidly diminished until it was insignificant when the next batch was brought in.

Provisional reports have been circulated to members, with the following titles :—

No. 5. The soaking process ; liming process ; bating ; chrome tanning ; moulds in tan liquors.

6. Action of sulphides and caustic soda on skins.

7. Structural differences in leather, made from dried, raw and salted hides.
8. Relation between colour and acidity in vegetable tanning.
9. Report on a theory of chrome tanning.
10. Structural characteristics of swelling and plumping.
11. Effects of moulds and other micro-organisms on vegetable tan liquors.

Dr. Pickard explained the chief features of provisional report No. 6. Both light leather manufacturers and others frequently have great difficulty in removing short hairs from skins after liming. Microscopical investigations show that sodium sulphide solutions dissolve the hair outside the skin, and also attack the hair follicle near the hair root, but the portion immediately below the surface of the skin is not attacked, and hence arises some of the difficulty in unhairing. The Research Association has found that by treating the skins with a solution of caustic soda prior to the sulphiding, the action of the sulphide on the portion of the hair follicle immediately below the surface of the skin is improved and the trouble arising from short hairs is minimised.

The controversy around the subject of bating[33] has become very keen during this year. J. A. Wilson and G. Daub,[34] in a critical study of the bating process, state that the elastin is present in two layers of the skin between the epidermis and the hair roots, and in the flesh tissue. It is completely removed by 0·01% pancreatin when the hydrogen ion concentration is $p_H=7{\cdot}5$—$8{\cdot}5$, and by 0·1% pancreatin at $p_H=5{\cdot}5$—$8{\cdot}5$. The rate of the removal of elastin from calf-skin depends on the concentration of enzyme and the time of digestion. A commercial bate was found to have no digestive action on elastin at any concentration, probably owing to the presence of too much woody fibre. J. T. Wood[35] states that although the elastin is completely removed from the skins bated by trypsin for a sufficiently long time (about twenty-four hours), in practice the bating is not continued to this point, but is carried on for only about 2–6 hrs. The elastin is only partly removed in this time, but the skins make good leather. He believes that it is not necessary, or even desirable, for the whole of the elastin to be removed or dissolved in order to let the skin down, but that it is sufficient for the elastic fibres to be broken up or weakened in order that the desired suppleness may be obtained. Dr. Pickard,[36] speaking at the lectures delivered at the Leathersellers' Hall in December, affirmed that bating did not remove the elastin but merely removed plumping and separated the fibres. Bating was quite reversible and it was not necessary to destroy the elastin. The encircling bands around the fibre bundles and around the fibrils were not elastin, and their nature was, as yet, unknown, but they were apparently not affected by the bating process. J. T. Wood questioned whether from the point of view of bating the action of swelling and plumping was reversible. The Röhm and Haas Co.[37] have published several observations on the histology of bated skins. All authors agree that the bating or puering process effects the deliming of the skins. The Röhm and Haas Co. agree with the views of Rosenthal, Wood, and Marriott that while the effect of the bate on the elastin is undoubtedly one of its important functions it is not yet established that it is the primary function of the bate; the essential effect of the bate on the elastin fibres is probably something considerably short of complete digestion, while there is every indication that a function of equal importance is the digestion and removal to some extent of the cementing or interfibrillary substance. The Röhm and Haas Co. have had a number of calf-skins and goat-skins limed, cut in half, one half bated with manure bates, and the other half with an enzyme bate; sections of the treated halves showed that a considerable amount of elastin was still present in both products. The results did not vary greatly between the enzyme bate and the manure bate. The attempt to remove all the elastin from calf-skins results in loose leather and considerable pipiness. A very fine series of photomicrographs is appended to the publication and the elastin fibres show up very clearly in all the bated specimens.

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[33] *Ann. Repts.*, 1921, **6**, 386.

[34] *J. Ind. Eng. Chem.*, 1921, **13**, 1137 ; *J.*, 1922, 68A.

[35] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 97.

[36] *Leather Trades Rev.*, 1922, 1022.

TANNING, TANNING MATERIALS, ETC.

There have been no startling discoveries of new tanning materials, but several workers have drawn attention to many materials which are being overlooked. W. R. Atkin and K. H. Hassan[38] have made a report on the qualitative and quantitative analysis of ten Indian tanning materials, *viz.*, Tarwar (*Cassia auriculata*) bark, amaltas, sundri bark, mohani bark, goran, amla bark, itsha bark, babul, dhawa leaves, divi-divi pods, sumach leaves and pomegranate kernel, all of which contain useful amounts of tannin. The hemlock trees of the Western States of North America are rapidly becoming exhausted and American tanners have been compelled to look around for fresh sources of supply. R. H. Clark and H. T. Andrews[39] have analysed numerous samples of freshly-cut western hemlock (*Tsuga heterophylla*) bark and spruce (Sitka) bark. The tannin content of freshly-cut western hemlock bark varied from 9·0% to 15·5%, and that of the spruce from

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[37] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 542.

[38] *J. Soc. Leather Trades Chem.*, 1921, **5**, 347 ; *J.*, 1922, 24A.

[39] *J. Ind. Eng. Chem.*, 1921, **13**, 1026; *J.* 1922, 67A.

12·0% to 17·5%, calculated on the dry substance. A comprehensive survey of the tanning resources of Western Australia was commenced in December, 1920, by the Forest Products Laboratory of the Institute of Science and Industry in Australia, with the object of collecting information about Western Australian barks which might be suitable for tanning. Over 170 samples have been analysed.[40] Karri bark (*Eucalyptus diversicolor*) has an average tannin content of about 20% ; it tans quickly and gives a light-coloured leather. The manufacture of a karri tanning-extract has been commenced.

One of the members of the staff of the Forest Products laboratory has reported[41] on the possibilities of marri kino (Red gum from *Eucalyptus colophylla*) as a tanning material. It contains 68–70% of matter absorbed by hide powder. It is very sparingly soluble, but it possesses an objectionable red colour and yields a brittle leather. There has been a proposal[42] to manufacture a tanning extract by treating dry peat extract with weak alkali. J. A. Pilgrim[43] has criticised the paper by B. B. Dhavale and S. R. Das,[44] because they ground the goran bark and then sifted it, whereas in practice the coarsely ground material always contains some fine powder, which is very rich in tannin. The solutions extracted were not always of analytical strength, and from corrections he has made it would appear that the 60–mesh material yielded most tannin. B. B. Dhavale and S. R. Das[45] have found the optimum temperature for the extraction of tannin from sundri (*Heritiera minor*) bark of " official size " to be 65°–70° C.

A great deal of attention has been devoted to the plumping of hides in the early stages of sole leather tanning. F. C. Thompson, K. Seshachalam, and K. H. Hassan[46] have analysed different tanning materials under conditions of varying acidity. The results show that the time of filtration, colour, content of tannin, and insoluble matter, all vary considerably with alterations in the hydrogen ion concentration. W. R. Atkin[47] has made a theoretical study of the factors influencing the plumping of hides in tan liquors. He states that the hide combines with acids to form hide-acid compounds, which can ionise and so exert osmotic pressure, thus tending to cause the hide to swell. Neutral salts and solutions of tannins tend to repress the swelling, and he suggests that tanners should determine the total acidity, the hydrion concentration, and the degree of swelling of hide powder in the tan liquors. E. C. Porter[48] prepared solutions of different hydrion concentrations and showed that a maximum swelling of hide powder was obtained at $p_H=2{\cdot}4$, a minimum at $p_H=4{\cdot}8$ and a second maximum at $p_H=12{\cdot}5$. Porter has repeated his work this year[49] and confirmed his previous results. He has also determined the amount of hide substance dissolved at the different hydrion concentrations, and he finds that there is practically no hydrolyses until the maximum of swelling is passed. Less than 3% of hide substance is dissolved by decinormal solutions in 24 hrs. It is evident that there is very little hydrolytic action in the tan liquors. W. Moeller[50] has carried out a large number of determinations of the hydrolytic effects of lactic and butyric acids on hide substance, and finds that not more than 6% of hide substance is hydrolysed by $N/2$ solutions of lactic acid in four weeks, and 4·6% by $N/2$ solutions of butyric acid E. C. Porter [51] has devised the following test for determining the swelling power of tan liquors: 0·5 g. of hide powder (30–60 mesh) is placed in a 120 c.c. graduated flask, so devised that it has a long neck graduated in one-tenth c.c. to accommodate the last 20 c.c. The hide powder is covered with 100 c.c. of the tan liquor to be tested, the flask stoppered with a rubber stopper, shaken at intervals and allowed to stand 24 hrs. After this, the flask is inverted for 2 hrs. to allow the swollen hide to settle down into the neck. The flask is smartly tapped on the bench for 30 secs., and the volume of swollen hide powder is then read off and compared with that given by other tan liquors.

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[40] *Leather World*, 1922, 291.

[41] *J. Soc. Leather Trades Chem.*, 1921, **5**, 384 ; *J.*, 1922, 67A.

[42] *Leather World*, 1922, 744.

[43] *J. Soc. Leather Trades Chem.*, 1922, **6**, 255 ; *J.*, 1922, 828A.

[44] *Ann. Repts.*, 1921, **6**, 389.

[45] *J. Soc. Leather Trades Chem.*, 1922, **6**, 311 ; *J.*, 1922, 907A.

[46] *Ibid.*, 1921, **5**, 389 ; *J.*, 1922, 68A.

[47] *Ibid.*, 1922, **6**, 138 ; *J.*, 1922, 475A.

A committee[52] of the American Leather Chemists' Association has reported on the modified Claflin method[53] for the direct measurement of the plumping power of tan liquors: 10 g. of hide powder is shaken for 10 mins. with a measured volume of the tan liquor, the contents transferred to a funnel plugged with absorbent cotton-wool, and the filtrate collected in a graduated cylinder. At the end of 40 mins., when the dripping has ceased from the filtration, the volume of the filtrate is noted and the difference between the volume of tan liquor taken and the filtrate obtained is a measure of the plumping power.

The colour of tan liquors has been shown by J. A. Wilson and E. J. Kern [54] to be influenced by their acidity. They prepared tan liquors from gambier and quebracho, and found that both had the same colour at $p_H=3{\cdot}0$, unless previously exposed to the air.

[48] *Ibid.*, 1921, **5**, 268; *J.*, 1921, 781A.
[49] *Ibid.*, 1922, **6**, 83.
[50] *Z. Leder- u. Gerb.-Chem.*, 1921-2, **1**, 153; *J.*, 1922, 426A.
[51] *Loc. cit.*
[52] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 341.
[53] *Ann. Repts.*, 1921, **6**, 398.
[54] *J. Ind. Eng. Chem.*, 1921, **13**, 1025; *J.*, 1922, 68A.

The change in colour of these tan liquors with varying acidity was found to be completely reversible if the liquors had not been exposed to the air for a time. Dr. Pickard reported on certain tests in this connexion at the lectures[55] delivered in December, on behalf of the British Leather Manufacturers Research Association. Solutions of different tanning materials were prepared, the solution of each material divided into seven portions, and the hydrion concentrations of these adjusted to $p_H=1$ to $p_H=7$, thus forming a series. A series of pieces of pelt of similar p_H values were procured and tanned in the solution of the same p_H value. The results showed that the colour of the finished leather depended on the p_H value of the tan liquors. If it was less than $p_H=4$ the finished leather was very dark and again when the tan liquor was slightly alkaline $p_H=8$. The line of demarcation between bad colour with excessive acidity and good colour was at the same p_H value for all the different materials, and it was reported that the Leather Manufacturers' Research Association had proposed the use of a special indicator, to enable tanners to determine the correct and most suitable acidity for their tan liquors.

G. Vie[56] points out that chestnut wood contains acetic acid which is volatilised during the evaporation of the wood extract, and can be recovered by passing the vapours through a scrubber containing sodium carbonate or milk of lime. It is possible to recover 13 lb. of acetic acid for every 100 lb. of extract produced. A. Harvey[57] has summarised the different purposes to which spent tanwood waste can be put. It can be distilled to yield acetic acid, mixed with lead nitrate and lime to form briquettes, mixed with bitumen to produce a roofing material, employed in paper-making, the manufacture of oxalic acid, wood tar, charcoal, and methyl alcohol, and for the reduction of bichromate for one-bath chrome tanning liquors.

K. C. Srinivasan[58] has analysed numerous samples of the bark of South Indian wattles (*Acacia decurrens*), showing tans 39·3–44·1% and non-tans 7·1–13·0%, which compares very favourably with the wattle barks of Australia and Africa. The optimum temperature of extraction is 60° C.; the tannin content increases with the age of the tree and leather tanned with it is soft and pliable.

Several patents have been granted for the production of tanning materials from waste sulphite-cellulose lye[59] and from vegetable tanning materials by condensing with sulphonic acids of aromatic hydrocarbons,[60] and improved apparatus has been devised for extracting and concentrating tanning materials.[61] F. Langford[62] mixes the wood of *Sesquoia sempervirens* with aluminous earths and water, treats with sulphur gases, and obtains a tanning material by further treatment. H. C. Reed[63] finds that the presence of calcium sulphate in water used for extracting tanning materials results in a slight loss of tannin, but the non-tans are not increased to the extent that would be expected. Analyses show a loss in tannin, but an increase in insoluble matter which may not mean a loss of tannin in actual practice. There may be a loss, however, owing to the repressive action of the dissolved salts upon the swelling of the hide.

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[55] *Loc. cit.*

[56] *J. Amer. Leather Chem. Assoc.*, 1921, **16**, 641; *J.*, 1922, 24A.

[57] *J. Soc. Leather Trades Chem.*, 1922, **6**, 24; *J.*, 1922, 150A.

[58] *Leather Trades Rev.*, 1922, 178.

[59] E.P. 171,136; *J.*, 1922, 225A; G.P. 347,201; *J.*, 1922, 384A; U.S.P. 1,414,312; *J.*, 1922, 477A.

SYNTHETIC TANS.

A large number of patents have been granted during the year for the manufacture of new and improved synthetic tans. Gerb- und Farbstoffwerke H. Renner u. Co.[64] oxidise sulphonated and condensed derivatives of cyclic hydrocarbons or phenols or acid resin, by means of potassium bichromate. H. Renner and W. Moeller[65] use coumarone-resins as the raw material for sulphonation and condensation. Acid sulphites are allowed to react below 100° C. on aromatic hydroxy-compounds in the presence of formaldehyde.[66] Di- and polyhydroxybenzenes, their homologues and substitution products containing at least one free para-position to the hydroxyl group, can be condensed with acetaldehyde or formaldehyde to form soluble tanning agents.[67] Aryl alkyl ethers, derived from halogenated aliphatic hydrocarbons containing 16 carbon atoms, by treatment with phenols or naphthols, can be sulphonated to produce a soluble synthetic tan.[68] Heavy coal-tar oil, tar phenols, phenol, creosote, etc. may be sulphonated, condensed with formaldehyde, neutralised, and mixed with chromium, iron, or aluminium chlorides,[69] or the neutralisation may be effected by means of compounds of aluminium or chromium or both,[70] or with compounds of other heavy metals.[71] Naphthalene and other polycyclic aromatic hydrocarbons and carbazole have been sulphonated and condensed with glycollic acid to produce a tanning agent.[72]

[60] E.P. 148,897 ; *J.*, 1922, 224A.

[61] E.P. 178,138-9 ; *J.*, 1922, 476A.

[62] U.S P. 1,390,796 ; *J.*, 1922, 782A.

[63] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 26 ; *J.*, 1922, 150A.

[64] E.P. 146,167, 146,182 ; *J.*, 1922, 185A.

[65] E.P. 148,750 ; *J.*, 1922, 185A.

[66] E.P. 154,162 ; *J.*, 1922, 263A ; E.P. 154,153 ; *J.*, 1922, 303A.

[67] G.P. .44,033 ; *J.*, 1922, 427A.

[68] G.P. 344,878 ; *J.*, 1922, 427A.

[69] E.P. 156,749 ; *J.*, 1922, 476A.

[70] E.P. 156,254 · *J.*, 1922, 602A.

[71] E.P. 156,670 ; *J.*, 1922, 774A.

[72] E.P. 158,521 ; *J.*, 1922, 775A.

R. B. Croad, G. E. Knowles, and H. M. McArthur and Co., Ltd.[73] have patented the condensation of 2 mols. of an aromatic hydroxy compound with 1 mol. of formaldehyde in presence of an oxide, hydroxide, carbonate, or bicarbonate of an alkali or alkaline-earth metal, ammonia, or a salt of a strong base with a weak acid. The product is sulphonated and may then be further condensed, if desired.

A very pleasing feature of this year in connexion with synthetic tans has been the widespread efforts to enlighten the leather trade as to the possibilities and effects of the use of these new materials. G. E. Knowles read a paper on "Synthetic Tannins and their uses in Leather Manufacture" before the North-Western section of the Society of Leather Trades Chemists.[74] He emphasised the importance of securing the right product free from excessive content of sulphuric acid and also the failure of the official method of tannin analysis as a method of testing the tanning properties of synthetic tannins. He urged tanners to judge samples by pelt tests in 1–5% solutions of the synthetic tannin. S. Kohn, J. Breedis, and E. Crede[75] divide synthetic tannins into "combination" and "adsorption" tans. Some contain compounds which combine chemically with the hide substance, but the products are not very stable or insoluble, and show a lower resistance to washing. The definition of "combination" tan should include some limits of stability and insolubility of the compound with collagen. The tanning value of synthetic tannins lies more in the increased efficiency they produce in vegetable tannins with which they are mixed than in their own tanning power. The acidity of the solution greatly influences the state of the tannin. At zero acidity the whole of the tannin is present as "adsorption tan," at the correct acidity as "combination tan," because the sample does not then contain any sodium sulphonates which follow the law of adsorption.

MINERAL TANNAGES.

Very little progress has been made in regard to the general procedure in tanning with chromium salts. The leather section of the C.W.S. Research Dept., Manchester, has published numerous papers on chrome tanning which are gradually revealing the nature of this process. A. Glover and G. Martin[76] have patented the use of dried whey for reducing mixtures of bichromates and acid, whilst D. Burton and A. Glover[77] have patented the use of tea-dust as a reducing agent in the manufacture of one-bath chrome tanning

[73] E.P. 182,823-4; *J.*, 1922, 774A.

[74] *J. Soc. Leather Trades Chem.*, 1922, **6**, 19.

[75] *J. Amer Leather Chem. Assoc.*, 1922, **17**, 166; *J.*, 1922, 336A.

[76] E P. 182,289; *J.*, 1922, 641A.

[77] E.P. 184,360; *J.*, 1922, 774A.

liquors. The use of an alkali or alkaline-earth carbonate in conjunction with an alkali or alkaline-earth salt of the lower fatty acids for neutralising chrome-tanned leather prevents over-neutralisation.[78] A similar mixture has been found suitable for iron- or aluminium-tanned leathers also.[79] A patent has been granted[80] during the year for the tanning of hides with ferric salts dissolved in solutions containing formic acid. Formaldehyde and sulphite-cellulose extract may also be added. D. Burton[81] has made several valuable studies on the chrome-tanning process. He draws attention to the influence exerted by the initial basicity figure, age, temperature, rate of increase in strength, and rate of neutralisation of the liquor on the feel of the resulting leather. The acidity of the liquor affects the boiling test and is influenced by the presence of neutral salts. "Ageing" improves the leather. The properties of a leather depend on the condition of the fibre at the moment of fixation of the chromium, the nature of the salt on the fibre, the kind of combination with the pelt and the mechanical treatment used for softening the leather. In a further study,[82] D. Burton discusses the swelling power of a chrome liquor and confirms the favourable influence exerted by organic substances in it. A. M. Hey[83] has tanned pieces of pelt with formaldehyde solutions at different p_H values. Alkali is not necessary, but the tannage proceeds most satisfactorily if the pelt is slightly alkaline ($p_H=7{\cdot}8$), and the formaldehyde solution $p_H=7{\cdot}2$.

There have been a few additions to our knowledge of tanned leather. More even dyeing of glacé leather can be ensured by previously mordanting with gambier neutralised with borax.[84] Tanning oils and fat-liquoring agents have been prepared by mixing phenol and resins obtained by distilling hydroxy-fatty acids.[85] W. Moeller[86] has described the action of hot water on various types of leather. Leathers of low-resistance to water yield a large amount of soluble gelatinous matter. Iron-tanned leathers[87] have a very small water-resistance figure, over 95% of the hide substance being hydrolysed in one case. Leathers tanned with synthetic tans[88] are much less resistant to hot water than vegetable- or mineral-tanned leathers and are similar to formaldehyde-tanned leathers. The British Leather Manufacturers' Research Association have isolated the chromium salt which is the active tanning agent in chrome tanning. They find that it can exist in two isomeric forms, one of which forms chrome soaps, which are responsible for 50–90% of the spues on chrome leathers. P. Hampshire[90] has classified the different spues appearing on leathers, and describes one spue caused by sodium sulphate, which he was able to dissolve out of the leather and reproduce on an unaffected piece of chrome leather.

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[78] G.P. 352,285, 353,130 ; *J.*, 1922, 722A, 774A.

[79] G.P. 353,131 ; *J.*, 1922, 774A.

[80] G.P. 349,363 ; *J.*, 1922, 641A.

[81] *J. Soc. Leather Trades Chem.*, 1922, **6**, 157 ; *J.*, 1922, 511A.

[82] *Ibid.*, 1922, **6**, 226 ; *J.*, 1922, 640A.

[83] *Ibid.*, 1922, **6**, 131 ; *J.*, 1922, 476A.

[84] G.P. 346,694 ; *J.*, 1922, 249A.

[85] G.P. 354,165 ; *J.*, 1922, 774A.

[86] *Z. Leder- u. Gerb.-Chem.*, 1921-2, **1**, 47 ; *J.*, 1922, 185A.

[87] *Ibid.*, 1921-2, **1**, 166 ; *J.*, 1922, 426A.

[88] *Ibid.*, 1921-2, **1**, 100 ; *J.*, 1922, 303A.

ANALYSIS.

The analysis of tanning materials and the analysis of leather are subjects of much agitated discussion at present. The degree of acidity has a very important influence on the colour, absorption, and effects of a tan liquor and its accurate determination is a matter of urgency. The Procter lime-water method is no guide and the p_H value is a safer guide. H. C. Reed and T. Blackadder[91] recommend the Claflin method[92] for measuring the plumping value of tan liquors. F. L. Seymour-Jones[93] has experimented with baryta as a substitute for lime-water in the Procter method, but finds no advantage. A committee of the American Leather Chemists Association[94] propose the use of a modified immersion type of colorimeter for measuring the colour of tannin solutions. The official method of tannin analysis has been subjected to severe criticisms, but further work has confirmed the opinion of many that it is a very good method in general, only requiring minor modifications to improve it instead of the drastic revision suggested by J. A. Wilson and E. J. Kern.[95] A. W. Thomas and M. W. Kelly[96] have shown that gambier solutions give a steady increase in adsorption with increase in the concentration of tannin solution used, which fact is used by G. W. Schultz[97] to controvert the Wilson-Kern proposals. Continental chemists are dissatisfied with the present official method of tannin analysis. J. Schneider[98] advocates the use of aliquot weighed portions of all solutions instead of measured portions. Dry chromed hide powder gives good results. L. Pollak[99] has modified the official shake method by using double and treble detannisations, a longer period of shaking, and a larger amount of hide powder, and by the filter bell method. The shake method with two detannisations gave a higher percentage of tans

[90] *Bureau of Bio-Technology Bull. No.* 6, 1922.

[91] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 109; *J.*, 1922, 302A.

[92] *Loc. cit.*

[93] *J. Soc. Leather Trades Chem.*, 1922, **6**, 393.

[94] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 20C; *J.*, 1922, 476A.

[95] *Ann. Repts.*, 1921, **6**,

[96] *J. Ind. Eng. Chem.*, 1922, **14**, 292; *J.*, 1922, 383A.

[97] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 348; *J.*, 1922, 641A.

[98] *J. Soc. Leather Trades Chem.*, 1922, **6**, 234; *J.*, 1922, 641A.

[99] *Collegium*, 1922, 125; *J.*, 1022, 773A.

than the official shake method. He concludes that the official shake method gives less than the true tannin content, and the filter bell method more. V. Kubelka and F. Berka[100] advocate the re-adoption of the filter bell method, but it is extremely unlikely that their arguments will have any effect. H. C. Reed and T. Blackadder[101] consider that the detannisation would be more complete if the solution was acidified with formic acid, less powder was employed, and it was shaken for a longer period of time with a stronger solution of the tannin. F. C. Thompson[102] has made a valuable suggestion for estimating the soluble matter of tannin solutions by allowing the insoluble particles to settle out and then evaporating 50 c.c. from the upper layer of the liquor. This includes as soluble matter particles below a certain size, but eliminates the uncertainties of filtration, and the personal factor in judging optical clearness.

Two important factors in the analysis of vegetable-tanned leathers have been the subject of much discussion this year, *viz.*, the extraction of oils and fats and the determination of the water-soluble matter. The discrepancies between the amount of extract removed from leather by chloroform and petroleum spirit, have been found to exist in chrome tanned leathers,[103] and British chemists have been strongly urged to adopt chloroform as the official solvent for extracting oils and greases. Members of a committee of the American Leather Chemists Association, however, have extracted various leathers with petroleum spirit and then with chloroform, and only about 25% of the chloroform extract has proved to be fat.[104] They incline to the opinion that the error involved in using chloroform is greater than that caused by the inefficiencies of petroleum spirit. A. M. Hey[105] shows that the presence of moisture in leather greatly affects the amount of extract obtained ; the influence is more apparent in the case of chloroform. G. W. Schultz[106] has summarised the present position very fairly by stating that petroleum spirit extracts too little, and chloroform too much, and he suggests two extractions, one with each solvent, if necessary. The last word has not been said, however, on the subject for there is evidence to confute some of the arguments advanced by the advocates of petroleum spirit.

A committee[107] of the French section of the Society of Leather Trades' Chemists has proposed a new method of determining the water-soluble matter in a vegetable-tanned leather, in which 5 g.

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[100] *Collegium*, 1922, 85, 143, 167 ; *J.*, 1922, 773A.

[101] *J. Soc. Leather Trades Chem.*, 1922, **6**,

[102] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 158 ; *J.*, 1922, 336A.

[103] *J. Soc. Leather Trades Chem.*, 1922, **6**, 97 ; *J.*, 1922, 303A.

[104] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 292.

[105] *J. Soc. Leather Trades Chem.*, 1922, **6**, 385.

[106] *Ibid.*, 1922, **6**, 389.

[107] *J. Soc. Leather Trades Chem.*, 1921, **5**, 313 ; *J.*, 1921, 859A ; 1922, **6**, 302 ; *J.*, 1922, 907A.

of rasped leather is extracted with 250 c.c. of distilled water for 16 hrs. at the ordinary temperature. W. J. Chater and D. Woodroffe[108] have shown that after the water-soluble matter has been extracted from vegetable-tanned leathers by the "official" method, there still remains an additional 10–30%, which can be removed by further extraction. A committee of the American Leather Chemists Association[109] has reported on the determination of water-soluble matter in leather and advocates extraction at a lower temperature, 25° C.

There have been attempts in certain quarters to discredit the results obtained by the chemical analysis of leather on the grounds that it is inaccurate and very variable. The chemical analysis, however, is the most consistent property of leather. Mechanical and physical tests are much more variable. If leather is properly sampled the results are very reliable, as R. C. Bowker and E. L. Wallace[110] have shown. L. Jablonski[111] states that no portion of a side is an average of the whole.

The determination of free mineral acid in leather requires modification since syntans and sulphonated oils contain sulphonic groups which are reported as free mineral acid by the Procter-Searle method. C. van der Hoeven[112] recommends extracting a weighed quantity of finely-divided leather with sodium dihydrogen phosphate for some hours. The total SO_4 is estimated in the extract and neutral sulphates in the ash. W. R. Atkin[113] states that sodium chromate is formed when the Procter-Searle method of determining free acid is applied to chrome leather and the error is corrected by titrating the sodium chromate with sodium hydroxide and making a correction. D. Burton, A. Glover, and R. P. Wood[114] have evolved a new method of determining the basicity of chrome tanning liquors by oxidising a known volume of the liquor with hydrogen peroxide and 25 c.c. of $N/1$ sodium hydroxide. The oxidised solution is diluted and part used for the chromium determination and part for the acidity. The method obviates the adsorption of sodium hydroxide by the precipitated chromium hydroxide. D. Woodroffe and R. E. Green[115] have devised a modified method of determining the amount of alkali salts in chrome leather, which is ashed, treated with strong sulphuric acid, the excess evaporated off, the residue ignited, the soluble sulphates extracted with boiling water, and estimated with barium chloride.

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[108] *J. Soc. Leather Trades Chem.*, 1922, **6**, 247 ; *J.*, 1922, 828A.

[109] *J. Amer. Leather Chem. Assoc.*, 1922, **17**, 220 ; *J.*, 1922, 476A.

[110] *Ibid.*, 1922, **17**, 217 ; *J.*, 1922, 476A.

[111] *Collegium*, 1922, 53, 96 ; *J.*, 1922, 773A.

[112] *Ibid.*, 1921, 458 ; *J.*, 1922, 68A.

[113] *J. Soc. Leather Trades Chem.*, 1922, **6**, 89 ; *J.*, 1922, 303A.

[114] *Ibid.*, 1922, **6**, 92 ; *J.*, 1922, 302A.

[115] *Ibid.*, 1922, **6**, 222; *J.*, 1922, 641A.

THEORY OF TANNING, ETC.

There is very little to report on the chemistry of the tannins. The work of E. Fischer is being consolidated and supported by fresh investigations on natural tannins.[116] A crystalline tannin has been isolated[117] from the leaves of *Acer ginnala*, and named acertannin $C_{20}H_{20}O_{13}$. It has been hydrolysed into gallic acid and aceritol, and is probably a sugar ester. K. Freudenberg and his pupils have continued their investigations and have succeeded in hydrolysing numerous natural tannins by means of tannase, the preparation of which from growths of *Aspergillus niger* they have carefully described.[118] By its aid they have hydrolysed chlorogenic acid, isolated a new sugar from hamameli-tannin, and investigated the tannins in chestnut and oak. They have also reduced flavanone and isolated various stereoisomeric catechins.[119] K. Freudenberg and E. Vollbrecht[120] have isolated a tannin from German oak, which contains 23–25% of combined ellagic acid, and 5% of combined dextrose, and an amorphous acid, quercussic acid. K. Freudenberg and W. Scilasi[121] have confirmed the doubts as to the homogeneity of Chinese tannin.

Numerous workers have studied the reaction between tannins and gelatin and pelt or hide substance. A. G. Brotman[122] finds that the amount of formaldehyde fixed by gelatin depends on the concentration of the jelly. O. Gerngross[123] claims that the influence of formaldehyde on the adsorption of alkalis by hide powder proves there is a chemical change in tanning. W. Moeller[124] explains away this influence and affirms his adherence to a colloidal theory of tanning. W. Moeller[125] has also shown that the absorption of tannin by hide powder is independent of the concentration and volume, and depends merely on the absolute amount of tannin present. A. W. Thomas and M. W. Kelly[126] have determined the time and concentration factors in the combination of tannin with hide substance for quebracho and gambier. Quebracho showed a maximum, but gambier gave a steady increase of absorption with the increase in the concentration of tannin solution used.

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[116] *Trans. Chem. Soc.*, 1922, **121**, 23 ; *J.*, 1922, 184A ; *Helv. Chim. Acta*, 1922, **5**, 108 ; *J.*, 1922, 184A.

[117] *Ibid.*, 1922, **121**, 66 ; *J.*, 1922, 184A.

[118] *Collegium*, 1921, 468 ; *J.*, 1922, [illegible]7A.

[119] *Ber.*, 1922, **55**, 1734, 1748 ; *J.*, 1922, 601A.

[120] *Ibid.*, 1922, **55**, 2420 ; *J.*, 1922, 906A.

[121] *Ibid.*, 1922, **55**, 2813 ; *J.*, 1922, 906A.

[122] *J. Soc. Leather Trades Chem.*, 1921, **5**, 363 ; *J.*, 1922, 25A.

[123] *Collegium*, 1921, 489 ; *J.*, 1922, 149A.

[124] *Z Leder- u. Gerb.-Chem.*, 1921-2, **1**, 54 ; *J.*, 1922, 337A.

[125] *Ibid.*, 1921-2, **1**, 28 ; *J.*, 1922, 184A.

[126] *J. Ind. Eng. Chem.*, 1922, **14**, 292 ; *J.*, 1922, 383A.

D. Burton and his co-workers[127] have shown that neutral salts retard the penetration of the chromium into the pelt, and raise the basicity of the liquors. F. C. Thompson and W. R. Atkin[128] suggest the existence of a negatively charged colloidal complex in chrome tanning solutions, which would bring the explanation of chrome tanning into line with that of vegetable tanning, *viz.*, the combination or co-precipitation of the positively charged collagen by the negatively charged colloidal tanning material.

Gelatin, Glue, etc.

W. Moeller[129] has tanned gelatin with formaldehyde, quebracho, and chrome tanning liquors, and finds that part of the gelatin is coagulable, and part remains in solution. A Scala[130] finds that salts are absorbed by gelatin up to a maximum and independent of the presence of other salts in the solution. R. Wintgen and H. Vogel[131] have investigated the gelatin-hydrochloric acid equilibrium and conclude that gelatin acts as a mono-acid base of molecular weight 885; β-glutin behaves similarly and has about one-half the molecular weight.

A. Kuhn[132] states that the swelling of gelatin in solutions of acids reaches a maximum at lower concentrations with strong acids and higher concentrations with weak acids. The swelling is the result of hydration, sol formation, hydrolysis, dehydration, and precipitation. W. Moeller[133] has confirmed Kuhn's work and finds that some acids, notably butyric acid, cause a diminution in the amount of hydrolysed gelatin. The swelling and hydrolytic effects of mineral acids differ from those of organic acids, and the action of acetic acid differs from that of lactic and butyric acids. H. G. Bennett[134] maintains his lyotrope theory of swelling, but the evidence against his views seems overwhelming. R. H. Bogue[135] re-states his theory as to the fibrillar structure of gelatin-water systems and quotes evidence in support of it. D. J. Lloyd[136] has shown that hydrochloric acid decreases the gelling power of gelatin, which passes through a maximum at $p_H=2-3$. Sodium hydroxide slightly decreases the gelling power between $p_H=10-12$, and completely prevents gelation above that figure. S. E. Sheppard, S. S. Sweet, and A. J. Benedict[137] find that the rigidity of demineralised gelatin jellies is not much affected by changes in hydrion concentration, but the addition of small amounts of potash alum has a marked effect; this agrees with the results of A. Gutbier, E. Sauer, and F. Schelling.[138] Bone glue is not so sensitive to the influence of the addition of alum. The clarification of glue is always accompanied by a deterioration, as shown by a decrease in the viscosity. J. and R. F. Loeb[139] divide colloidal solutions into those which are easily precipitated by small quantities of neutral salts and others which require larger quantities. Casein dissolved in caustic soda solutions belongs to the second type, gelatin to the first type. The swelling and viscosity of gelatin solutions[140] increase with a decrease in silica content, owing to a change in hydrion concentration. They reach a maximum at $p_H=8·5$; the jelly consistence is solid between $p_H=4·7$ and $p_H=8·0$, soft at $p_H=8·5$, and liquid at $p_H=9·0$.

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[127] *J. Soc. Leather Trades Chem.*, 1922, **6**, 6; *J.*, 1922, 149A; 1922, **6**, 157; *J.*, 1922, 511A.

[128] *Ibid.*, 1922, **6**, 207; *J.*, 1922, 560A.

[129] *Z. Leder- u. Gerb.-Chem.*, 1921-2, **1**, 90; *J.*, 1922, 303A.

[130] *Ann. d'Ig.*, 1921, **3**, 289; *J.*, 1922, 150A.

[131] *Kolloid-Zeits.*, 1922, **30**, 45; *J.*, 1922, 150A.

[132] *Kolloid-Chem. Beih.*, 1921, **14**, 147; *J.*, 1922, 111A.

[133] *Z. Leder- u. Gerb.-Chem.*, 1921-2, **1**, 160, 183; *J.*, 1922, 560A.

[134] *J. Soc. Leather Trades Chem.*, 1922, **6**, 223; *J.*, 1922, 641A.

[135] *J. Amer. Chem. Soc.*, 1922, **44**, 1343; *J.*, 1922, 560A.

[136] *Biochem. J.*, 1922, **16**, 530; *J.*, 1922, 907A.

Prior to 1914 the glue pieces from large Indian tanneries were worked up in Germany, but the war interfered with this, and the Government sought to establish a glue industry in India itself. The difficulties were many, the temperature was troublesome, both for setting purposes and for obviating putrefaction. G. J. Fowler, K. C. Srinivasan, and V. S. Chinnaswami[141] have determined the concentration of acid in glue-liquor which prevents the growth of liquefying bacteria. The addition of phenol or formaldehyde to the glue-liquor prevents putrefaction, but not the growth of moulds. E. T. Oakes and C. E. Davis[142] have described a "plunger" method of measuring gel-strength, in which a plunger is attached to the under-side of a balance-scale pan, on which is placed a beaker. The whole is counterpoised and water added to the beaker until the plunger is forced into the gel placed below. The maximum gel-strength coincided in p_H value with the maximum increase in viscosity. Data were obtained in favour of the gelatin-acid combination theory. C. E. Davis, E. T. Oakes, and H. H. Browne[143] find that the maximum viscosity of gelatin solutions is reached at $p_H=3·0$—3·5 at 25° C., and after solutions have stood 24 hrs. The density[144] of a gelatin solution can be expressed in g. per c.c. by the density of water at the same temperature, plus $(x \times 0·0029)$ where x is the percentage concentration of gelatin by weight. F. A. Elliot and

[137] *J. Amer. Chem. Soc.*, 1922, **44**, 1857; *J.*, 1922, 908A.
[138] *Kolloid-Zeits.*, 1922, **30**, 376; *J.*, 1922, 601A.
[139] *J. Gen. Physiol.*, 1921, **4**, 187; *J.*, 1922, 69A.
[140] *J. Ind. Eng. Chem.*, 1922, **14**, 32; *J.*, 1922, 262A.
[141] *J. Indian Inst. Sci.*, 1921, **4**, 107; *J.*, 1922, 426A.
[142] *J. Ind. Eng Chem.*, 1922, **14**, 706; *J.*, 1922, 721A.
[143] *J. Amer. Chem. Soc.*, 1921, **43**, 1526; *J.*, 1921, 898A.
[144] *Ibid.*, 1922, **44**, 464; *J.*, 1922, 337A.

S. E. Sheppard[145] describe experiments on the determination of the gold value of 17 different commercial gelatins.

Numerous patents[146] have been taken out for making glue and gelatin, which refer chiefly to improved apparatus for extracting. A liquid glue is prepared by mixing glue with an alkaline-earth silicate or thiourea.[147]

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[145] *J. Ind. Eng. Chem.*, 1921, **13**, 699 ; *J.*, 1921, 859A.

[146] E.P. 156,645 ; *J.*, 1922, 602A ; E.P. 166,896 ; *J.*, 1922, 869A ; G.P. 351,243 ; *J.*, 1922, 561A ; U.S.P. 1,421,620 ; *J.*, 1922, 641A ; E.P. 166,896 ; *J.*, 1922, 869A ; E.P. 156,646-7 ; *J.*, 1922, 384A.

[147] U.S.P. 1,394,653-4 ; *J.*, 1922, 860A.

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SOILS AND FERTILISERS.

By H. J. PAGE, M.B.E., B.Sc., A.I.C.,

Chief Chemist, Rothamsted Experimental Station, Harpenden.

IN this report, attention will be mainly confined to fertiliser and soil questions which are likely to be of direct interest to the technical agricultural chemist dealing with practical problems; as in former years, the more theoretical aspects of the subject are discussed in the Report to the Chemical Society.

During the past year the financial depression in the agricultural industry, of which signs were already evident in the previous year, has become markedly accentuated. Indeed, it is no exaggeration to say that the crisis bids fair to equal in severity that through which British agriculture passed in the 'eighties. The severe slump in the wholesale prices of agricultural products, which has not been accompanied by an equal fall in the prices which the farmer has to pay for his feeding-stuffs and manures, has brought large number of farmers to bankruptcy; those who escape this fate are largely laying down arable land to grass, and restricting their expenditure in every possible direction. Apart from the larger economic aspects of the crisis—of the gravity of which evidence is afforded by the appointment by the Government of a Departmental Committee to "inquire into the methods of selling and distributing agricultural, horticultural, and dairy produce," and of a "Tribunal of Investigation" to "inquire into the methods which have been adopted in other countries during the last fifty years to increase the prosperity of agriculture, and to secure the fullest possible use of the land for the production of food, ... and to advise as to the methods by which these results could be achieved in this country,"[1]—the direct effects on the fertiliser industry are likely to be considerable.

FERTILISERS.

The results of modern experiments on the use of fertilisers necessarily call for critical consideration in this connexion.

In this period of enforced economy, the pronouncement of Lawes during the last period of depression, that "high farming is no remedy for low prices," was bound to be recalled. Lawes' dictum was based on the results of Rothamsted experiments, which showed that, for the dressings of fertilisers used in these experiments on wheat, the extra return obtained by the use of an increased amount of fertiliser, although profitable in a period of high prices, was not sufficient to balance the increased cost of the larger dressing in a period of low prices.[2] In the discussion at the Hull Meeting of the British Association (joint meeting of the Economics and Agriculture Sections), and in the subsequent correspondence in the press, this fact was used by the upholders of the view that the farmer's only remedy at the present time was to draw in his horns, to lay arable land down to grass, and generally to scale down production to a low level. That this view is not necessarily a sound one, in the light of more recent work, is maintained by Sir E. J. Russell,[3] who points out that the fertiliser dressings applied in the experiments used by Lawes in support of his contention were all, even the smallest, much larger than would be used in practice, even in most intensive farming, and the results are therefore not really applicable. Recent results with smaller dressings of fertilisers, within the range of those used in practice, seem to indicate that, so far from gradually falling off from the outset in accordance with the law of diminishing returns, the increase in produce obtained from one moderate increase in the amount of fertilisers used, is less than that obtained from a further equal increase in the dressing; in other words, if yield is plotted as ordinate against amount of fertilisers applied, as abscissa, the initial part of the curve bends towards, and only later does it bend away from, the axis of ordinates. This is a very interesting point, which, if definitely established, may have most important effect on the economic utilisation of fertilisers; the results of further experiments on the matter will be awaited with great interest.

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[1] See *The Times*, Dec. 12, 1922.

J. Hendrick[4] has published a useful discussion of the fertiliser positions before, during, and since the war, including statistics of production and consumption. It is perhaps not sufficiently generally realised that the manufacture of fertilisers, no less than that of dyestuffs, is a "key industry." The manufacture of sulphuric and nitric acids, and ammonia, which the dyestuff industry can utilise in time of war for the production of explosives, is dependent for its existence in time of peace mainly on the fertiliser industry.

Hendrick also quotes results of manurial experiments in Scotland to test the relative value of the newer types of nitrogenous, phosphatic, and potassic fertilisers.

J. G. Lipman has given a useful review of the fertiliser position in the United States.[5]

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[2] See Hall and Russell, "The Book of the Rothamsted Experiments" (1917), pp. 46 and 47.

[3] *J. Min. Agric.*, 1922, **29**, 752, 836.

[4] *Trans. High. and Agric. Soc. Scotland*, 1922, **34**, 93-114; *J.*, 1922, 537R.

[5] *J.*, 1922, 233R.

A new journal, the *Zeitschrift für Pflanzenernährung und Düngung*, has been started in Germany, under the editorship of Professors O. Lemmermann and P. Ehrenberg. It is published in two parts, the one dealing with the more academic side, and the other dealing with practical fertiliser problems. Its future will be watched with interest.

Although in certain cases, such as that of sulphate of ammonia, the demand is still greater than the supply, in general there is no scarcity of fertilisers, and competition has resulted in low prices.

Nitrogenous Fertilisers.

Nitrogen-Fixation.—Nitrogen-fixation is a factor of ever-increasing importance in relation to nitrogenous fertilisers. Several new factories in Europe and the New World are reported. Thus, in Rumania (Transylvania) cyanamide is being manufactured, for conversion into ammonia, which is then exported to Austria for oxidation, though this stage also will later be carried out in Rumania; natural gas is used for heating.[6] A new German company, the Cosag Kontinentale Stickstoffwerke A.-G., is erecting a factory at Galling in Austria.[7] In British Columbia the American Nitrogen Products Company is operating a plant at Lake Buntzen for the production of nitrates by an electrical method,[8] while the Electro-Chemical Company of Canada intends to erect a plant for the production of calcium nitrate, with a capacity equivalent to over 3000 tons of nitric acid per annum.[9] A description of the construction and operation of the U.S. Government synthetic ammonia plant at Sheffield, Ala. (now no longer running) has been published comparison being made with the German factory at Oppau.[10] A report has been issued of the inquiry into the disastrous explosion which destroyed the Oppau factory, but no definite conclusion was come to.[11] It has, however, been established that a mixture of equal parts of ammonium sulphate and nitrate can be detonated by a very strong initiator.[12] The Oppau factory has already been rebuilt, and although German production of fixed nitrogen is not yet sufficient to leave a margin for exportation after home demands have been satisfied, there seems to be little doubt that at the present rate of development, German nitrogen products will before long be a serious factor in the world markets, particularly if the mark remains near its present low level.[13] Considerable attention was attracted to the international aspects of Germany's fixation industry by J. Harker's paper at the British Association (Section B).[14] Harker stated that by the end of 1922 Germany will have at her disposal an internal capacity for the production of fixed nitrogen of about 500,000 tons annually, a total so colossal that she will be entirely independent of all importation. The paper should also be consulted for a good survey of the various nitrogen fixation processes. F. Häusser has published a description of his explosion process for nitrogen fixation.[15] This process was also dealt with by C. J. Goodwin, at the British Association (Section B).[16]

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[6] *Chim. et Ind.*, Jan., 1922; *J.*, 1922, 178R.

[7] *J.*, 1922, 266R.

[8] *J.*, 1922, 453R.

[9] *J.*, 1922, 420R.

[10] *Chem. and Met. Eng.*, 1922, **26**, 245, 307, 359, 411, 463.

[11] *Chem.-Zeit.*, Oct. 5, 1922; *J.*, 1922, 451R.

[12] *Chem. Ind.*, Jan. 16, 1922; *J.*, 1922, 62R.

[13] C. Matignon, *Chim. et Ind.*, July, 1922; *J.*, 1922, 400R.

Nitrates.—The Chilean nitrate industry is still suffering from the severe slump in the second half of 1921.[17] At the end of June, 1922, only 33 factories were working, and exports for the first six months of the year had fallen to less than 300,000 tons, compared with nearly 800,000 tons for the same period in 1921.[18] A recovery early in 1923 is, however, anticipated. The continuous growth of competition between natural nitrate and competitive artificial products is well shown by the following figures[19] :—

	Consumption.			
	1894.	1904.	1913-14.	1921.
	%	%	%	%
Chilean nitrate	73	66	56	33
Competitors	27	34	44	67

The life of the Chilean nitrate deposits now being worked is estimated to be at least a hundred years, and the discovery in Chile of an extensive new deposit in Tarapaca, estimated to be 772 square miles in area, and 2–3 feet thick, with a content of sodium nitrate of 20–40%,[20] further postpones the time when agriculture will depend exclusively on chemical or biological fixation for its supply of combined nitrogen.

Norwegian (synthetic) nitrate sales declined badly in 1921, and a loss of 1·31 million kroner was incurred.[21] During the present year the position has improved somewhat, and it is estimated that the production of nitrate of lime for the year ending December 21st, 1922, will be 170,000 metric tons. A patent for rendering sodium or calcium nitrate non-hygroscopic has been taken out.[22]

Ammonium Salts.—Sulphate of ammonia is still the standard nitrogenous fertiliser in this country, and the home stocks—depleted by the coal strike and large exports in 1921, and by relative inactivity

[14] *J.*, 1922, 387R.
[15] *J.*, 1922, 254R.
[16] *J.*, 1922, 394R.
[17] *Bd. of Trade J.*, April 13, 1922 ; *J.*, 1922, 226R.
[18] *J.*, 1922, 460R.
[19] *J.*, 1922, 271R.
[20] *U.S. Com. Rept.*, Dec. 19, 1921 ; *J.*, 1922, 102R.
[21] *Chem. Ind.*, Jan. 23, 1922 ; *J.*, 1922, 86R.
[22] R. G. Browning and H. G. T. Boorman, E.P. 180,180 ; *J.*, 1922, 562A.

of the coke ovens owing to slackness in the steel industry—were entirely sold in 1922, at a greatly reduced price, which was forced on the vendors by the low prices ruling for nitrate of soda. Over half of the sulphate of ammonia now produced by the Sulphate of Ammonia Federation is of the neutral quality, sold on a basis of $25\frac{3}{4}\%$ ammonia.

The utilisation of cyanamide as a source of ammonia forms the basis of an American process, which turns out mono-ammonium phosphate under the name of "Ammophos." A similar process forms the subject of German patents, whereby cyanamide is treated with sodium bisulphate solution, and the resulting sodium ammonium sulphate is treated with superphosphate to give sodium ammonium phosphate for use as a concentrated mixed fertiliser.[23] The Badische Company has patented the preparation of a mixed fertiliser containing nitrate and carbonate of ammonia, with superphosphate.[24]

On purely theoretical grounds, there is much to be said for ammonium bicarbonate as a fertiliser; when other ammonium salts are applied to the soil they are converted into bicarbonate, their acid residues merely serving to hasten the loss of lime from the soil, or to make the soil "sour." Moreover, the bicarbonate is cheaper to produce than the sulphate or the chloride. The practical obstacle is the volatility of this salt, but according to W. Gluud[25] there is no serious loss, casks losing only 2·75% by weight, and resined paper bags only 0·5%, in 30 days. This loss is stated to be probably only carbonic acid, the sesqui-salt being first formed. Details are given of the process of manufacture for gasworks or coke ovens using the indirect or semi-indirect processes, and it is stated that even allowing 5% for loss on storage, cost figures show a saving as compared with present processes of ammonia recovery.

The utilisation of crude gas liquor as a fertiliser has been discussed,[26] and also forms the subject of a patent.[27]

Cyanamide.—Although cyanamide is the cheapest synthetic nitrogen compound to produce, and although its manurial value, if not equal to that of sulphate of ammonia, is usually not seriously less, its future as a fertiliser is not hopeful. This is, in part, due to its tendency to polymerise to the toxic dicyanodiamide, and also in part to the dusty and caustic nature of the product hitherto put on the market, which makes it an unpleasant and unpopular substance to apply to the land. Some of the processes designed to do away with the latter drawback, increase the former. The use of cyanamide in mixed fertilisers, for which it is in many ways well suited, was likely to be seriously hindered by the statement that it is gradually converted into the polymer in the presence of superphosphate.[28] This statement, however, could not be confirmed by two independent workers[29]; indeed, it is now stated that in fertiliser mixtures dicyanodiamide, if present, is depolymerised.[30] Nevertheless, the unpopularity of cyanamide seems to be indicated by the cessation of its manufacture in Norway,[31] and by the number of attempts which are being made to improve it, more especially to render it non-dusty. The following are examples.

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[23] Baumbach und Co., G.P. 299,131 and 300,022; *J.*, 1922, 858A, 870A.

[24] Badische Anilin- und Soda-Fabrik, G.P. 351,130; *J.*, 1922, 512A.

[25] *Chem.-Zeit.*, 1922, **46**, 693, 715; *J.*, 1922, 722A.

[26] J. Mews, *Gas- und Wasserfach*, 1922, **65**, 123; *J.*, 1922, 263A.

[27] Ges. für Landwirtschaftlichen Bedarf, and R. Mandelbaum, E.P. 153,006; *J.*, 1922, 151A.

A process which has been patented in Germany consists in mixing the calcium carbide with volcanic rock silicates before treatment with nitrogen. The product is said to be non-caustic, non-dusty, and to contain soluble potash.[32] In other German patents the cyanamide is treated with tar or other oils, or with fats,[33] or with sulphite-cellulose pitch.[34] In America a patent has been taken out for the treatment of cyanamide with water and solid or liquid carbon dioxide,[35] while a Swedish company has taken out a British patent for a process, whereby the cyanamide is treated with warm 25% nitric acid and then granulated in a current of hot air.[36] The object of all these processes is to obtain a dustless product.

P. Mazé[37] has obtained promising results by the application of cyanamide mixed with ten times its weight of peat.

Urea.—A more hopeful use for cyanamide seems to be its employment as a raw material for the manufacture of ammonia, or of urea, which continues to attract attention as a promising fertiliser. The conversion to urea may be effected[38] by warming at 80° C. an acidified solution of cyanamide, to which is added as catalyst a paste containing 83% of ferrosoferric oxide (such as is obtained in the reduction of nitro-compounds by iron); the transformation to urea is complete in one hour, and no dicyanodiamide is formed.

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[28] R. N. Harger, *J. Ind. Eng. Chem.*, 1920, **12**, 1111; *J.*, 1921, 93A.

[29] W. S. Landis, *ibid.*, 1922, **14**, 143; *J.*, 1922, 385A. J. E. Breckenridge, *ibid.*, 1922, **14**, 145; *J.*, 1922, 385A.

[30] *J.*, 1922, 292R.

[31] *J.*, 1922, 222R.

[32] Rhenania Verein Chem. Fabriken A.-G. and G. A. Voerkelius, G.P. 345,815; *J.*, 1922, 264A.

[33] W. Schwarzenauer, G.P. 306,237. W. Schrauth, G.P. 353,493; *J.*, 1922, 775A.

[34] A. Mann, G.P. 313,129; *J.*, 1922, 829A.

[35] J. M. A. Stillesen, U.S.P. 1,386,445; *J.*, 1922, 870A.

[36] Stockholms Superfosfat Fabriks Aktiebolag, E.P. 168,070; *J.*, 1922, 950A.

[37] *Comptes rend.*, 1922, **175**, 1093; *J.*, 1923, 110A.

[38] Farbwerke vorm. Meister, Lucius, u. Brüning, G.P. 301,278; *J.*, 1922, 521A.

Other patents dealing with this conversion may be mentioned[39]; one of them is apparently the same as a process now being operated in Switzerland by the Société des Produits Azotés,[40] in which the urea is produced in admixture with superphosphate, the product being known as "Phosphazote." The cost of manufacture of this material is said to be by no means high, and it is becoming popular in France for the manuring of vineyards.

An alternative method for the production of urea is by the dehydration of ammonium carbonate, which is readily obtained from carbon dioxide and ammonia. C. Matignon and M. Fréjaques have studied the influence of conditions and of catalysts on the conversion,[41] and the Badische company has patented a process in Germany and in this country.[42] The same problem has been investigated in America by N. W. Krase and V. L. Gaddy.[43] Urea is rapidly hydrolysed in the soil, but even if for any reason the change were slow, no direct harm to the plant would result, as even at a concentration of 1% urea is non-toxic to plants.[44] It seems by no means unlikely that the manufacture of nitrogenous fertilisers from "synthetic" ammonia will ultimately take the form of its conversion into urea instead of into ammonium salts. Carbonic acid is cheaper than sulphuric or hydrochloric acid, and ammonium nitrate, besides being under a cloud since the Oppau explosion, has not caught on as a fertiliser. Moreover, urea is a more concentrated fertiliser than any ammonium salt, so that for equal nitrogen value freight charges are less.

Fertiliser Tests.—The results of the field trials which are being carried out in this country at Rothamsted and a number of other centres on the relative value of the newer nitrogenous fertilisers are not yet sufficiently available for trustworthy conclusions to be drawn. In America, the results of experiments carried out at the Massachusetts Experiment Station, using sulphate of ammonia each year since 1889, gave, for equal amounts of nitrogen, a value of 95 to sulphate of ammonia against 100 for nitrate of soda.[45] At the Mississippi Experiment Station nitrate of soda, nitrate of ammonia, and cyanamide were effective in the order named.[46] In Germany (Brunswick) for potatoes sulphate of ammonia gave the best results on light soil, but sulphonitrate was best on loam;

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[39] Soc. d'Etudes Chim. pour l'Industrie, E.P. 151,597, 151,598, 154,562, 154,563, 159,853, 159,854; *J.*, 1922, 111A, 112A.

[40] *J.*, 1922, 331R.

[41] *Chim. et. Ind.*, 1922, **7**, 10[illegible]; *J.*, 1922, 646A. See also K. C. Bailey, *Comptes rend.*, 1922, **175**, 279; *J.*, 1922, 685A.

[42] Badische Anilin- und Soda-Fabrik, G.P. 301,279; E.P. 145,060 *J.*, 1922, 488A.

[43] *J. Ind. Eng. Chem.*, 1922, **14**, 611; *J.*, 1922, 610A.

[44] T. Bokorny, *Biochem. Zeits.*, 1922, **132**, 197; *J.*, 1922, 950A.

[45] F. W. Morse, *Mass. Sta. Bull.*, 1921, **204**, 83.

[46] H. B. Brown and J. F. O'Kelly, *Mississippi Sta. Rept.*, 1921, 16.

nitrate of soda gave the best yields of sugar beet on loam, while for tobacco on light land urea, sulphonitrate of ammonia, and cyanamide were effective in the order named; on meadowland cyanamide and sulphate of ammonia were each slightly better than nitrate of soda.[47] Bicarbonate of ammonia gave good results with various crops, approaching and sometimes equalling sulphate of ammonia.[48] [49] In Denmark, experiments in 1916–19, comparing the value of nitrate of soda, sulphate of ammonia, and cyanamide for nine different crops on four different soils, showed, taking nitrate of soda at 100, for sulphate of ammonia figures of 64 to 94, and for cyanamide figures of 23 to 85, the best results with cyanamide being obtained with turnips, oats, and cabbages.[50]

Analysis.—Methods have been described for the estimation of total, nitrite, and nitrate nitrogen in fertilisers,[51] and for the determination of total nitrogen in mixtures of cyanamide and nitrates.[52]

Phosphatic Fertilisers.

The main interest still centres round the agricultural value of the newer types of basic slag, and of raw mineral phosphates. A useful summary of the position in this country with regard to the use of phosphatic fertilisers in agriculture is given by Russell.[53] On the Continent, there was in France a good demand for superphosphate, bone meal, and slag, in all cases in excess of supply,[54] while in Germany, where in the past there has been a tendency to neglect phosphatic fertilisers, their value for maintaining yields is being increasingly recognised, and supplies were twice as abundant as in the previous year.[55]

Superphosphate.—The consumption of superphosphate in this country is on the increase, the sales for the year ending September 30th, 1922, being over 12% higher than for the previous year. New factories are projected in South Africa[56] and Tasmania,[57] Nauru phosphate being used in the latter. In Belgium the output is still below the pre-war figure of 230,000 tons.[58] A further patent has been taken out for the use of nitric instead of sulphuric acid in the manufacture of superphosphate[59]; also a patent for the concentration by froth-flotation of the mineral phosphate used in the ordinary process.[60] Several patents have been taken out in the United States for new plants for the manufacture of superphosphate.[61]

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[47] O. Nolte and A. Gehring, *Deut. Landw. Presse*, 1922, **49**, 31.

[48] Gluud, *loc. cit.*

[49] *J.*, 1922, 399R.

[50] P. Bolin, *Meddel. Centralanst. Försöksv. Jordbouksomrädet.*, 1921, No. 217; *Expt. Sta. Record*, 1921, **47**, 322.

[51] F. Mach and F. Sindlinger, *Z. angew. Chem.*, 1922, **35**, 473; *J.*, 1922, 908A. See also *Landw. Vers.-Stat.*, 1922, **99**, 95.

[52] K. D. Jacob and W. J. Geldard, *J. Ind. Eng. Chem.*, 1922, **14**, 1045; *J.*, 1923, 24A.

[53] E. J. Russell, *J. Min. Agric.*, 1922, **29**, 234.

[54] *Chem. Ind.*, Aug. 28, 1922; *J.*, 1922, 406R.

[55] *Chem. Ind.*, May 29, 1922; *J.*, 1922, 353R.

[56] *S. Afr. J. Ind.*, March, 1922; *J.*, 1922, 219R.

[57] *Ind. Austr.*, April 6, 1922; *J.*, 1922, 264R.

[58] *J.*, 1922, 318R.

Basic Phosphates.—There is still great uncertainty as to the relative value of the open-hearth basic slags, as compared with the now almost unobtainable Bessemer basic slag, but evidence is gradually accumulating regarding the influence of soil and climatic conditions on the results obtained. The Second Interim Report of the Permanent Committee on basic slag set up by the Ministry of Agriculture, has been issued.[62] There it is pointed out that although the demand for basic slag is on the increase, the output is not, and in 1920 and 1921 basic slag was imported from the Continent in increasing amounts (38,000 tons in 1921). Little, if any, change is likely to be made in blast-furnace or steel furnace procedure, with the object of improving either the output or the quality of slag. The reason for this is apparent, when it is remembered that for a ton of steel, worth £10 in 1921, the value of the 4 cwt. of slag produced is, before grinding, only 2s. The Committee, therefore, accepts the fact that the output of slag is less, and likely to remain less, than could advantageously be used by farmers, and is turning its attention to the possibility of increasing the effectiveness of basic slag, or of finding effective substitutes in ground mineral phosphates. A summary is given of the results of field trials, but no definite conclusions can yet be drawn from the results, owing to the abnormal drought in 1921, which prevented the slags from producing their full effect. The committee concludes, however, that the official solubility test needs revision. The most extensive field experiments carried out with the new slags are those by G. S. Robertson in Essex. A monograph embodying the results of these experiments has been published.[63] These results go to show that on heavy soils (boulder clay and London clay) the high-soluble open-hearth slags are as effective on meadow land as the old Bessemer slag, while the low-soluble, fluorspar slags, although less effective than the high-soluble slags, are still of considerable value, particularly in moist districts and on sour soils, and are far more effective than their solubility figures would suggest.

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[59] A.-G. für Anilin-Fabrikation, G.P. 355,180; *J.*, 1922, 829A.

[60] W. Broadridge and E. Edser, E.P. 171,155; *J.*, 1922, 26A.

[61] W. T. Doyle, U.S.P. 1,401,527; *J.*, 1922, 151A. T. J. Sturtevant, U.S.P. 1,403,820; *J.*, 1922, 187A. T. J. Sturtevant, U.S.P. 1,428,920-1,428,922; *J.*, 1922, 829A.

[62] *J. Min. Agric.*, 1922, **29**, 530.

[63] "Basic Slag and Rock Phosphates"; *J.*, 1922, 320R.

A. Demolon[64] has studied the rate of solution of calcium, magnesium, and manganese from various slags with various solvents. The calcium at first goes into solution very rapidly, and then only very slowly, while the manganese is easily soluble in 2% citric acid.

A valuable monograph on the phosphate deposits in the Empire has been published by the Imperial Mineral Resources Bureau.[65] Submarine deposits have been found off the coast of South Africa.[66]

It has already been mentioned that the Basic Slag Committee is considering the possibility of using ground mineral phosphates directly, as substitutes for basic slag, as is already widely done in the United States; the Empire resources of rock phosphate are much greater since the war, as the oceanic deposits in the Pacific are now available. The output from these deposits, which was 105,838 tons in 1919–20,[67] had risen to 364,251 tons for 1921–22, of which 73% went to Australia, 5% to New Zealand, 4% to the United Kingdom, and 18% elsewhere.[68]

Much of the Nauru phosphate that has reached this country has been put on the market in admixture with low-grade basic slag, but it remains to be seen whether such a mixture is a sound one. There is little doubt that in moist districts and on sour soils ground mineral phosphate is often at least equal in value to high-soluble basic slag, while in some cases even on sweet soils and in dry districts it is not much inferior, despite its lower citric-solubility; it appears to be always better than the low-soluble fluorspar slags. These results were obtained by G. S. Robertson in Essex,[69] on meadow land, and further experiments in Northern Ireland on the turnip crop tend to show Gafsa phosphate as equal to high-soluble open-hearth slag.[70] J. S. Marais[71] has carried out pot culture experiments on the relative "availability" of the phosphates of aluminium, iron, and calcium, and concludes that all three normal phosphates are equally available, but that the basic hydrated (mineral) phosphates of iron and aluminium are less so; this could be remedied by ignition. Lime increased the availability of aluminium phosphate, had no effect on the ferric compound, and reduced that of calcium phosphate. Assimilation was assisted by the active nitrification of urea. C. Brioux[72] also has investigated the relative value of the normal phosphates of iron, aluminium and calcium, in pot experiments. Mineral phosphates are more available to some crops than to others, and M. von Wrangell,[73] as a result of pot experiments with different plants, concludes that the power of any species to utilise the phosphorus of relatively insoluble mineral phosphates varies directly with the ratio of $CaO:P_2O_5$ in its ash. Of the fourteen species examined, the lowest phosphorus utilisation was shown by wheat and rye, and the highest by buckwheat. K. Mack[74] finds that insoluble phosphates are rendered soluble by colloidal humic acid, and that ammonium humate acts on phosphates of iron and aluminium to give soluble substances which appear to contain humic acid, phosphoric acid, and metal, in a complex anion; but he recommends the use of phosphates in conjunction with organic manures.

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[64] *Comptes rend.*, 1922, **174**, 1703; *J.*, 1922, 594A.

[65] "Phosphates, 1913-1919," Imperial Mineral Resources Bureau; *J.*, 1922, 10R.

[66] *S. Afr. J. Ind.*, Nov.-Dec., 1921; *J.*, 1922, 8R.

[67] *Col. Rep. Ann.*, No. 1088, 1921; *J.*, 1922, 65R.

[68] *Ind. Austr.*, Aug. 31, 1922; *J.*, 1922, 481R.

[69] See [62].

[70] G. Scott Robertson, *J. Min. Agric.*, 1922, **29**, 519, 600; *J.*, 1922, 484A

[71] *Soil Sci.*, 1922, **13**, 355; *J.*, 1922, 561A.

[72] *Comptes rend.*, 1922, **175**, 1096; *J.*, 1923, 110A.

Increasing attention is being directed towards the question of the influence of fineness of grinding on the availability of basic phosphates. It is obvious that the finer any material is ground (and therefore, the greater its surface) the more rapidly will it be attacked by chemical or physical solvents, and there is an increasing amount of evidence from field trials that basic phosphates give the best results when very finely ground. D. A. Gilchrist has summarised much of this evidence.[75] The reduction of mineral phosphates to a "colloidal" condition is the subject of a process patented in this country,[76] the material being suspended in much water, faintly alkaline, and subjected to the action of a special mechanical disintegrator run at a very high speed (1000–2000 r.p.m.). J. D. Tocher[77] has made a study of the influence of conditions on the solubility of rock phosphate in citric acid solution; he has also carried out field experiments on turnips with mineral phosphates.[78] He concludes that the only practical tests of the value of phosphatic fertilisers from the agricultural standpoint are: (1) total phosphatic content; (2) degree of fineness of grinding; (3) freedom from injurious substances and substances inhibiting plant growth. This is probably an overstatement, for although the physical state of the material is undoubtedly of great importance, there must be considerable chemical differences between, *e.g.*, a low-grade fluorspar slag and a phosphate rock such as Nauru, although we are still badly in need of information as to the exact nature of these differences.

T. Dieckmann and E. Houdremont[79] have determined the citric-solubility of various possible constituents; they find that tetracalcium phosphate, $4CaO,P_2O_5$, tricalcium phosphate, $Ca_3(PO_4)_2$, and calcium silicophosphate, $5CaO,P_2O_5,SiO_2$, are all over 90% soluble in 2% citric acid, but that oxyapatite, $3Ca_3(PO_4)_2,CaO$, has a solubility of only 67%, while fluorapatite, $3Ca_3(PO_4)_2,CaF_2$, is only 10·1% soluble, thus tending to confirm the earlier conclusions of Bainbridge.[80] They also find that the highly-soluble tetracalcium phosphate decomposes at 1000° C. or on slow cooling, giving the less soluble oxyapatite, whereas the silicophosphate is unaffected, and therefore they recommend that there should be sufficient silica in the slag to combine with the free lime. The common view that the phosphorus in basic slag is present only as tetracalcium phosphate, cannot be taken as satisfactorily established. The possible chemical effect of silica in facilitating phosphate assimilation may be indicated by the work of O. Lemmermann and H. Wiessmann,[81] who found that, in sand cultures, colloidal silicic acid produced the biggest increases in yield in cases in which insufficient phosphoric acid was present.

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[73] *Landw. Jahrb.*, 1922, **57**, 1; *J.*, 1922, 561A.
[74] *Chem.-Zeit.*, 1922, **46**, 73; *J.*, 1922, 186A.
[75] *J. Min. Agric.*, 1922, **29**, 706.
[76] H. O. Traun's Forschungslaboratorium G.m.b.H., E.P. 156,124; *J.*, 1922, 385A.
[77] *J. Agric. Sci.*, 1922, **12**, 125; *J.*, 1922, 512A.
[78] *Trans. High. Agric. Soc. Scotland*, 1922, **34**, 106.
[79] *Z. anorg. Chem.*, 1921, **120**, 129; *J.*, 1922, 304A.

Whatever may be the advantage of high solubility in basic phosphates, attempts continue to be made to render mineral phosphates soluble by means other than their conversion to superphosphate. Of these, the production in Germany of Rhenania phosphates[82] (referred to in last year's report, p. 410) is one of the most noteworthy. The composition of the product is stated to approximate roughly to that required by the formula $(CaO)_2{}^{K}_{Na}\!>O,P_2O_5$, the percentage composition being P_2O_5 15–25, K_2O and Na_2O 8–15 ($K_2O=8$), SiO_2 10–20, CaO 35–40. The citric-solubility is 80–90%, while 75% of the phosphorus is soluble in an aqueous solution of carbonic acid. Nearly one million tons has been sold, and the evidence of pot and field trials is stated to be favourable, its value being equal to or greater than that of basic slag.[83] Another method, which has been patented in the United States, is to briquette the phosphate with coal or other combustible material, and then roast.[84, 85] According to a process patented in this country[86] the phosphoric acid of mineral phosphates, bonemeal, or slag can be rendered citric-soluble merely by intimate grinding with salts of alkalis or alkaline-earths. In another process, fermenting plant material is mixed with iron ore containing phosphate; the filtrate is neutralised and absorbed in mineral matter.[87]

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[80] See *J.*, 1921, 124A, 156A. See also A. Scott and D. N. M'Arthur, *J. West of Scotland Iron and Steel Inst.*, 1922, p. 79.

[81] *Z. Pflanz. Düng.*, 1922, (A), **1**, 185.

[82] *Z. angew. Chem.*, Oct. 3, 1922; *J.*, 1922, 452R.

[83] F. Weiske, *Mitt. Deut. landw. Gesell.*, 1921, **36**, 667.

[84] E. C. Soper, U.S.P. 1,396,149; *J.*, 1922, 26A.

[85] *J.*, 1922, 292R.

[86] Eisenwerkges. Maximilianshütte, E.P. 186,223; *J.*, 1922, 909A

[87] R. Eberhard, E.P. 146,351; *J.*, 1922, 187A.

The use of sulphur oxidising bacteria in rendering mineral phosphates soluble is referred to later.

Analysis.—J. C. Vogel[88] has described a useful direct titration method for the determination of water-soluble P_2O_5 in superphosphate. R. Meurice[89] has studied the determination of calcium in natural phosphates. The preparation of the neutral solution of ammonium citrate which is used officially in America for determining citric solubility, has been standardised.[90]

Potassic Fertilisers.

A useful compilation of up-to-date information on the world's potash resources, with special reference to the British Empire, has been published.[91]

The competition between the French and the German potash interests, which is all to the good of the agriculturist, seemed likely to cease when it was reported that negotiations were in progress for the re-establishment of a monopoly,[92] but nothing came of these.[93] During 1921 the German syndicate began to feel the effects of French competition, especially in American markets.[94] German potash exports began to improve at the end of 1921, but at the beginning of 1922 they fell off,[95] only to improve again,[96] and to such an extent that the estimated foreign sales for 1922 are 1,250,000 metric tons,[97] thus for the first time exceeding the pre-war 1913 figure of 1,100,000 metric tons. This is largely due to the big reduction in prices of potash manures which took place last spring, and again later, bringing about a very considerable autumn trade, chiefly in kainit. The lowest grade potash salts are now materially cheaper than they have ever been before. The production of potash from the Alsatian mines, which suffered a set-back in 1921, more than recovered in 1922; in 1921 900,000 metric tons of crude salts (equals 110,500 metric tons K_2O) was produced, as compared with 1,350,000 metric tons of crude salts (230,000 metric tons of K_2O) in 1922. The latter figure is a record for these mines. The exports for the first nine months of 1921 and 1922 respectively were 366,577 and 706,698 metric tons of potash salts (equal to 85,037 and 169,684 metric tons of K_2O).

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[88] *J.*, 1922, 197T.

[89] *Ann. Chim. Analyt.*, 1922 (ii.), **4**, 198.

[90] C. S. Robinson, *J. Assoc. Off. Agric. Chem.*, 1921, **5**, 93; *J.*, 1922, 82A. See also *J.*, 1922, 428A.

[91] S. J. Johnstone, "Potash," Imperial Institute (John Murray, 1922); *J.*, 1922, 408R.

[92] *J.*, 1922, 377R.

[93] *J.*, 1922, 398R.

[94] *J.*, 1922, 178R.

[95] *J.*, 1922, 428R.

[96] *Deut. Bergwerks-Z.*, June 23, 1922; *J.*, 1922, 314R, 451R.

[97] *J.*, 1922, 536R.

Potash production in the United States, which fell off in 1919, revived somewhat in 1920, reaching a figure of 166,834 tons, an increase of nearly 50% over 1919.[98] The existence of extensive potash deposits in Western Texas has been confirmed, although their thickness is not yet known. A red salt containing 18–19% K_2O, probably polyhalite, has been found to be fairly widely distributed.[99]

The United States Government kelp plant at Summerland, California, now produces potash only as a by-product.[100] The recovery of potash as a by-product in the blast-furnace industry is still receiving some attention. It is calculated that in the United States 5·6 lb. of K_2O is volatilised for every ton of pig iron, giving an estimated total for all plants in the United States of 100,000 tons of potash annually, compared with 87,000 tons from the cement industry.[101] Flue-dust potash is still on the market in this country. Experiments have been carried out in the United States on the preparation from wool-scouring waste of a fertiliser containing 6% K_2O and 5% N, and it is hoped to put this on the market.[102]

The bulk of the American potash production is, however, derived from natural brine. After a year's closure, the American Trona Corporation is re-opening its potash plant at Searles Lake, California. The product will be put on the market at a price to compete with imported material.[103] The crude potassium chloride from this lake may contain as much as 25% of borax, and as such, is quite unsuitable as a fertiliser. A satisfactory method of eliminating this harmful impurity has now been worked out, and a high-grade muriate is produced, containing less than ½% borax, which is within the U.S. regulations limiting the borax content to a maximum of 0·5–1%.[104]

The utilisation of silicate rocks as a source of potash continues to receive attention, particularly in the United States, and also in Germany, several processes being patented.[105] It is stated that nitrate of potash from greensand is shortly to be put on the American market.[106] Shales containing 5% or more of K_2O are stated to occur in Illinois. If these are used in cement manufacture, and known methods of recovery applied, it is estimated that it would be possible to obtain a yield of 5·3 lb. of potash per barrel of cement.[107]

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[98] *U.S. Geol. Surv.*, Oct., 1921 ; *J.*, 1922, 8R.

[99] *Chem. and Met. Eng.*, 1921, **25**, 1179 ; *J.*, 1922, 32R.

[100] See No. 96.

[101] W. H. Ross and A. R. Metz, *J. Ind. Eng. Chem.*, 1922, **14**, 302.

[102] *J.*, 1922, 292R. See also F. P. Veitch, *J. Ind. Eng. Chem.*, 1922, **14**, 434 ; *J.*, 1922, 427A.

[103] *J.*, 1922, 265R.

[104] W. H. Ross and W. Hazen, *Chem. and Met. Eng.*, 1922, **27**, 167 ; *J.*, 1922, 706A.

[105] Chem. Werke. Rhenania, and A. Messerschmitt, G.P. 300,643 ; *J.*, 1922, 151A. A. H. Cowles, U.S.P. 1,408,169 ; *J.*, 1922, 305A. G. A. Blanc and F. Jourdan, U.S.P. 1,418,366 ; *J.*, 1922, 562A.

In the Far East potash is produced from seaweed to a moderate extent. Japan exported to the United States in 1920, 1143 tons of chloride and 834 tons of carbonate; small quantities of potash salts are also exported from China, the Dutch East Indies, and Straits Settlements.[108] It is suggested that the ash of the water-hyacinth, *Eichornia crassipes*, a common tropical weed, containing 7·5% of soluble K_2O, could be used in India and Burma as a potash manure.[109]

Despite the amount of attention that is thus still being devoted to the extraction of potash from industrial residues, silicate minerals, etc., especially in the United States, it is unlikely that much will ever come of this, with supplies from the German and Alsatian mines so abundant and cheap.

There is little or no precise information available regarding the relative manurial value of sulphate, high-grade chloride, and low-grade chloride of potash. In view of the fact that the German mines can produce either sulphate or chloride, while the Alsatian mines can only turn out chloride, this is a matter of some importance, and an extensive series of field trials on various crops at Rothamsted and other centres has been started.

Lesage[110] concludes, from water culture experiments, that natural sylvinite contains something else besides its chief constituents, potassium, sodium, and magnesium chlorides and calcium sulphate; a mixture of these salts in the same proportions as those in which they are present in natural sylvinite, gave results inferior to those obtained with the natural material.

It is stated that the crust-forming action of potash manure salts, especially kainit, is due to their magnesium content, which acts largely by causing mechanical cementation, rather than by causing deflocculation or chemical action.[111]

A further paper has appeared on the volumetric bitartrate method of determining potash.[112] Atkinson's perchlorate method has been found unsatisfactory.[113] A distillation method for the determination of borax in fertilisers has been described.[114]

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[106] *J.*, 1922, 131R.

[107] M. M. Austin and S. W. Parr, *J. Ind. Eng. Chem.*, 1921, **13**, 1144; *J.*, 1922, 140A.

[108] *Ch. of Com. J.*, May 19, 1922; *J.*, 1922, 294R.

[109] *Imp. Inst. Bull.*, **19**, 4; *J.*, 1922, 401R.

[110] P. Lesage, *Comptes rend.*, 1922, **175**, 992; *J.*, 1923, 110A.

[111] A. von Nostitz, *Landw. Versuchs-Stat.*, 1921, **99**, 27; *J.*, 1922, 186A.

[112] Macheleidt, *Woch. Brau.*, 1922, **39**, 23; *J.*, 1922, 200A.

Organic and Mixed Manures.

The preparation of so-called "artificial farmyard manure" from the fermentation of straw[115] has now passed out of the laboratory stage. A syndicate (the Agricultural Development Company) has been formed for the commercial exploitation of the process and large-scale demonstrations are being carried out on farms in various parts of the country. The value of the material is being thoroughly tested on the practical scale.[116]

A careful investigation of the nitrogen cycle in the activated sludge process of sewage purification, involving both laboratory and large-scale work, and of the manurial value of activated sludge, has been carried out.[117] The higher nitrogen content of the activated sludge as compared with ordinary sludge is found to be derived from the ammonia of the sewage; there is no evidence of nitrogen fixation. The cell-contents of the very large numbers of protozoa in well-activated sludge (about 1,000,000 per gram) may account for a large proportion of the extra nitrogen. Activated sludge produced at the Harpenden sewage works contained 5·5–6·8% of nitrogen calculated on the dried material, and the value was not affected by changes in the method of working. There is always a loss of nitrogen in the process, varying from 20% to 80%, according as conditions are favourable or the reverse. The proportion of total nitrogen in Harpenden sewage recovered in normal working was 15%, compared with 10% by precipitation and 4% by septic tanks, while by adopting special measures the recovery may be as high as 27%. Field experiments at Rothamsted with activated sludge made at the Harpenden sewage works showed that this sludge had a high manurial value in marked contrast with the old type sewage sludges previously tested.

The question of the utilisation of town refuse as a manure is being taken up. A useful summary of the position in this country is given by E. J. Russell.[118]

A valuable monograph has been published by A. Bruttini, in which the agricultural utilisation of waste materials and residues is treated exhaustively.[119] As usual, a number of patents have been taken out for the production of fertilisers from peat, waste materials, and so on, by chemical or fermentation methods. The value of many of these is not obvious.[120]

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[113] S. J. Watson, *Analyst*, 1922, **47**, 285.

[114] J. M. Bartlett, *J. Assoc. Off. Agric. Chem.*, 1921, **5**, 88; *J.*, 1922, 26A. See also W. H. Ross, *ibid.*, 1922, **5**, 440.

[115] See *Ann. Repts.*, 1921, **6**, 411; also *J. Min. Agric.*, 1921, **28**, 398.

[116] See, *e.g.*, G. H. Garrad, *Modern Farming*, August, 1922.

[117] E. H. Richards and G. C. Sawyer, *J.*, 1922, 62T.

[118] E. J. Russell, *J. Min. Agric.*, 1922, **29**, 685, 838.

[119] "Ramassage et Utilisation des Déchets et Résidus" (International Institute of Agriculture, Rome, 1922).

The alkaline permanganate method of estimating the "availability" of ammonia in organic manures has been investigated.[121]

Calcareous and Magnesian Materials.

The value of sea sand as a calcareous soil dressing, as used largely in Cornwall, has been discussed.[122] W. Mather[123] could observe no difference in the action of magnesian and non-magnesian limestone on crop yields or soil reaction; both rendered the aluminium in the soil relatively insoluble. No effect on plant growth could be observed from variations in the Ca/Mg ratio in the soil. R. H. Robinson and D. E. Bullis[124] found that chalk and lime produced different effects on different acid soils, when added so as to satisfy the Veitch "lime requirement." Laboratory examination showed that those soils that responded to lime gave a rapid nitrification on liming. Calcium sulphate was found to increase the soluble potash and magnesia in all soils.

O. Nolte could observe no benefit from the use of waste gypsum for the conservation of liquid manure.[125] The use of gypsum for the reclamation of "alkali" soils has been studied by P. L. Hibbard.[126] German patents have been taken out for the preparation of so-called fertilisers from magnesium compounds; it is not obvious that the products would be of much fertilising value.[127]

Sulphur as a "Fertiliser."

The work of J. G. Lipman and his associates at the New Jersey Experiment Station on the bacterial oxidation of sulphur, which has been going on since 1916, is being actively developed in the practical direction. The extraordinary organism, *Thiobacillus thiooxidans*, which is a most active oxidiser of elementary sulphur, can exist in a medium with a p_H of 0·58, and grows best in media at p_H=2·8–2·0. Treatment with sulphur in the presence of this organism is being advocated for several purposes, such as: (1) to control potato scab; (2) to reclaim black alkali soils; (3) to increase the availability of phosphates.[128] A patent has been taken out for the culture of the organism.[129]

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[120] *Peat*:—The Molassine Co., Ltd., and H. C. S. de Whalley, E.P. 173,276; *J.*, 1922, 187A. D. Lo Monaco, U.S.P. 1,402,638; *J.*, 1922, 151A. See also Mazé, *loc. cit.* *Organic refuse*:—C. L. Paynor, U.S.P. 1,398,113; *J.*, 1922, 71A. S. J. Smith, U.S.P. 1,402,102; *J.*, 1922, 187A. R. Balmer, U.S.P. 1,408,064; *J.*, 1922, 304A. Soc. Anon. Brevetti Beccari, E.P. 175,586; *J.*, 1922, 603A. D. Lo Monaco, E.P. 184,833; *J.*, 1922, 829A. *Nitrated carbohydrate*:—W. O. Snelling, Assr. to Trojan Powder Co., U.S.P. 1,410,037; *J.*, 1922, 338A. *Conditioning with halogen gases or with nascent hydrogen*:—D. Lo Monaco, U.S.P. 1,402,638; *J.*, 1922, 151A. C. A. Butt, U.S.P. 1,418,618; *J.*, 1922, 603A. *Artificial liquid manure*:—G. Cyliax, G.P. 355,038, 355,991; *J.*, 1922, 829A. *Fixation of nitrogen by carbonaceous material and gypsum*:—K. Niedenzu, E.P. 166,887; *J.*, 1922, 602A.

[121] C. S. Robinson and O. B. Winters, *J. Assoc. Off. Agric. Chem.*, 1922, **5**, 446.

[122] W. Borlase and A. Gregg, *J. Min. Agric.*, 1922, **29**, 591.

[123] *Soil Sci.*, 1922, **13**, 337; *J.*, 1922, 561A.

[124] *Ibid.*, 1922, **13**, 449; *J.*, 1922, 677A.

[125] *Ibid.*, 1922, **13**, 1[illegible]5; *J.*, 1922, 337A.

[126] *Mitt. Deut. landw. Ges.*, 1922, **37**, 41.

[127] B. Stollberg, G.P. 342,971; *J.*, 1922, 187A. C. Kroseberg, G.P. 353,371; *J.*, 1922, 723A.

S. A. Waksman[130] has demonstrated that by treating soil with sulphur, inoculated with the above organism, the acidity of the soil can be increased sufficiently to inhibit the growth of *Actinomyces scabies*, the organism responsible for potato scab.

W. Rudolfs[131] has studied the effect of treatment of black alkali soils with inoculated sulphur. The alkalinity of the soil was gradually reduced, but leaching is also needed, otherwise the dissolved salts still cause trouble. A marked effect on the flocculation and bacterial numbers of the soil was observed.

Perhaps the most striking results have been obtained in the work on the production of soluble phosphates from rock phosphate by treatment with sulphur.

In a liquid culture containing sulphur and tricalcic phosphate the sulphur-oxidising organism soon produces an acidity of about p_H=2·8, which is maintained until all the phosphate has been made soluble.[132] The same change occurs in a compost of soil, rock phosphate, and sulphur; monocalcium phosphate is stated to be first formed, and then to react with the tricalcic phosphate to give dicalcic phosphate.[133] W. Rudolfs, working in France, has studied the conditions best suited to the production of soluble phosphate from a compost of rock phosphate and sulphur with a slightly alkaline calcareous soil, with a view to make possible the application of the process on the manufacturing scale.[134] The same worker has found that iron pyrites can be similarly oxidised, and that this mineral seems to exert a catalytic influence in a soil-sulphur-phosphate compost, in presence of sulphate of ammonia.[135] Field experiments at the Mississippi Experiment Station on cotton demonstrated a considerable increase in yield, following treatment with raw rock phosphate and sulphur, though either alone had a depressing effect.[136] On the other hand, German experiments with oats and carrots on different soils gave disappointing results.[137] Possibly the right organisms were not present.

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[128] J. G. Lipman, S. A. Waksman, and J. S. Joffe, *Soil Sci.*, 1921, **12**, 475; *J.*, 1922, 187A.

[129] J. G. Lipman, E.P. 161,553; *J.*, 1922, 112A. See also J. S. Joffe, *Soil Sci.*, 1922, **13**, 161. S. A. Waksman, *Soil Sci.*, 1922, **13**, 329; *J.*, 1922, 561A.

[130] *Soil Sci.*, 1922, **14**, 61; *J.*, 1922, 870A.

[131] *Ibid.*, 1922, **13**, 215; *J.*, 1922, 427A.

[132] S. A. Waksman and J. S. Joffe, *J. Biol. Chem.*, 1922, **50**, 35; *J.*, 1922, 263A.

[133] J. S. Joffe, *Soil Sci.*, 1922, **13**, 107; *J.*, 1922, 338A.

[134] W. Rudolfs, *ibid.*, 1922, **14**, 37; *J.*, 1922, 870A.

[135] W. Rudolfs, *ibid.*, 1922, **14**, 135; *J.*, 1922, 949A.

Another aspect of the question is the possibility of actual deficiency of sulphur in a long cultivated soil. It is stated that in America 50–100% increase in crops of lucerne and other legumes has been obtained by using sulphur, and it is suggested that on such soils sulphur may be a limiting factor, so that crop increases obtained by the use of sulphate of ammonia or superphosphate, may be due to their sulphur content, rather than to their nitrogen or phosphoric acid.[138]

Carbon Dioxide as a Fertiliser.

The German work on this subject[139] has attracted considerable attention. The value of the system in greenhouse work is being critically investigated at one of the research stations in this country, and Riedel's process is being tried by several British nurserymen.

Electroculture.

The Electroculture Committee of the Ministry of Agriculture has published a preliminary account of the results so far obtained at Rothamsted, Lincluden, and the Harper Adams Agricultural College. The work is still proceeding, but there appears to be definite evidence of an increase in crop in field experiments, by the electrification of spring-sown oats and barley.[140]

SOILS.

Soil Moisture.

B. A. Keen has studied the evaporation of water from soil receiving artificials, unmanured soil, and soil receiving farmyard manure, and finds that the rate of evaporation decreases in the above order.[141] T. Deighton has investigated the electrical method of soil moisture determination; the relation found by American workers, *i.e.*, that the resistance varies inversely as the square of the moisture content, is concluded to hold good for moisture contents over 10%, but below this figure irregularities appeared.[142]

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[136] H. B. Brown and J. F. O'Kelly, *loc. cit.*

[137] Gerlach, *Mitt. Deut. landw. Ges.*, 1921, **36**, 726.

[138] *J.*, 1922, 292R.

[139] See last year's *Report*, p. 413.

[140] *J. Min. Agric.*, 1922, **29**, 792.

[141] *J. Agric. Sci.*, 1921, **11**, 433; *J.*, 1922, 69A.

[142] *Ibid.*, 1 22, **12**, 207; *J.*, 1922, 991A.

Water-Soluble Constituents.

A. F. Gustafson confirms the known effect of drying a soil in increasing the amount of water-soluble material. Soil kept moist, but not saturated, for nine weeks at ordinary temperature suffered little change in its content of water-soluble material. For pot culture work it is highly important that soils should be kept under strictly comparable conditions of moisture, temperature, and aeration.[143] From freezing point determinations C. E. Millar finds that the soluble matter in the top 6 in. of uncropped soil reaches a maximum in summer, and is low in early spring and late autumn. In the soil between 6 in. and 12 in. depth the soluble matter is low and suffers no seasonal fluctuation. Soluble matter tends to accumulate in the top quarter of an inch, especially in dry seasons, but cropping hinders this and also influences the value for the layer between ¼ in. and 6 in. depth.[144]

Soil Colloids.

N. M. Comber has brought forward further evidence in support of his hypothesis of the mechanism of the flocculation of clay soils by calcium hydroxide,[145] and has extended it to the characterisation of "fat" and "lean" clays.[146] He has also brought forward a modification of the present hypothesis regarding the mode of absorption of nutrient materials by the plant root, involving a more intimate and direct *rôle* of soil colloids in this process.[147] The adsorption of acid calcium phosphate by gels of iron oxide, alumina, and silica, in relation to the influence of soil colloids on the availability of salts, has been investigated by N. E. Gordon and E. B. Starkey.[148]

R. Sokol has described a method for the determination of colloidal clay in soils.[149] F. M. Scales and F. W. Marsh[150] have studied the measurement of the concentration of soil suspensions by an optical method.

Soil Reaction.

Much confusion has resulted in this field from the fact that several distinct factors are concerned in the development of so-called soil-acidity, and these are not always clearly distinguished. O. Lemmermann and L. Fresenius emphasise this point, and distinguish three types of soil acidity: (1) actual acidity of the soil solution, due to the presence of acids; (2) latent acidity developed in the presence of neutral salts, due to the liberation by basic exchange of readily hydrolysed iron and aluminium salts; (3) latent acidity developed in the presence of salts of weak acids with strong bases, the base being absorbed by the soil colloids and the acid left. Soil acidity must be considered in relation to the manurial treatment. Soils may have little active acidity, but marked latent acidity. With such soils no injurious effect due to acidity is observable unless dressings of salts such as potassium chloride are given.[151] The discrepancies observed between results of determinations by the various "lime requirement" methods depend largely on the fact that the principles of these methods involve the coming into action to different degrees of the above three and of other factors. V. Vincent[152] has shown that the difference in the lime-requirement values obtained in methods where calcium hydroxide and calcium bicarbonate are used is explicable by the fact that ferric hydroxide and hydrated silica are precipitated by the former, but not by the latter. E. A. Fisher[153] emphasises the need for taking into account the buffer action of the soil, by determining the change of p_H of soils on the addition of acids or alkalis, and studying the titration curve so obtained. The apparent p_H of the soil, as determined colorimetrically, is often influenced by the suspended matter present. D. J. Healy and D. E. Kanaker[154] have used the Clarke hydrogen-electrode vessel for determining the hydrogen-ion concentration of fresh and air-dried soils. The latter give higher values. Comber's test for sour soils has been used by R. H. Carr as the basis of a quantitative method for the determination of "lime-requirement,"[155] while Comber has devised a simpler modification of his original test, using an aqueous potassium salicylate solution instead of alcoholic potassium thiocyanate.[156]

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[143] *Soil Sci.*, 1922, **13**, 173; *J.*, 1922, 427A.

[144] *Ibid.*, 1922, **13**, 433; *J.*, 1922, 677A.

[145] *J. Agric. Sci.*, 1921, **11**, 450; 1922, **12**, 372; *J.*, 1922, 69A. See also *J.*, 1920, 793A.

[146] *J.*, 1922, 77T.

[147] *J. Agric. Sci.*, 1922, **12**, 363; *J.*, 1923, 110A.

[148] *Soil Sci.*, 1922, **14**, 1; *J.*, 1922, 870A.

[149] *Intern. Mitt. Bodenkunde*, 1921, **11**, 184; *J.*, 1922, 829A.

[150] *J. Ind. Eng. Chem.*, 1922, **14**, 52; *J.*, 1922, 263A.

Soil Analysis.

Mechanical and Physical.—G. W. Robinson[157] has developed a new method for determining the mechanical composition of soils and clays, depending on the determination of the concentration of settling suspensions for different values of the ratio of depth to time. The method gives results in good accord with those obtained by the present standard English method for the soils so far examined (palæozoic soils devoid of lime). The suitability for general use of the method, which is rapid, in marked contrast to the tediousness of the old method, is being critically examined at Rothamsted. The same author[158] has shown that a considerable proportion of the organic matter in humus soils can be oxidised away by the use of hydrogen peroxide, with a minimum of change to the mineral part of the soil. After such treatment, much higher "clay" figures are obtained than by the standard method of mechanical analysis, since in the latter the compound particles of a humus soil are not entirely broken down. C. L. Whittles[159] has discussed the classification of soils on the basis of their mechanical analysis, and has introduced a method of plotting the mechanical composition of soils in triangular co-ordinates. The formation of layers in clay suspensions has been studied by E. Ungerer,[160] who concludes that in any layer the particles are of uniform size, the space between the layers containing particles uniformly dispersed, and from the rate of rise or fall of the layers the size of the particles may be calculated according to Stokes' law. B. A. Keen and H. Raczkowski[161] have described a simple method for measuring the following properties of a soil: real and apparent specific gravity, pore space, water absorbed by unit volume, and volume expansion on saturation. The specific gravities vary inversely, and the other values directly, as the clay content of the soil.

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[151] *Z. Pflanz. Düng.*, 1922 (A), **1**, 12; *J.*, 1922, 384A.

[152] *Comptes rend.*, 1922, **175**, 1233; *J.*, 1923, 194A.

[153] *Nature*, 1921, **108**, 306. See also E. M. Crowther, *Trans. Faraday Soc.*, 1922, **17**, 317.

[154] *Soil Sci.*, 1922, **13**, 323.

[155] *J. Ind. Eng. Chem.*, 1921, **13**, 931; *J.*, 1922, 25A.

[156] *J. Agric. Sci.*, 1922, **12**, 370; *J.*, 1923, 110A.

[157] *Ibid.*, 1922, **12**, 306; *J.*, 1922, 990A.

Chemical Analysis.—The shortcomings of our present methods of chemical analysis of soils, in so far as they are intended, and not infrequently fail, to supply information as to the cropping power and manurial requirements of a soil, are by no means entirely the fault of the chemist. They depend more on the facts that the science of the soil is still in its infancy, or perhaps rather, its adolescence; and that our knowledge of plant nutrition does not yet enable us to say what are the minimal concentrations of the nutrient elements in the soil solution, below which the roots are incapable of absorbing them, nor how these values vary from one crop to another.

K. A. Vesterberg[162] has discussed this aspect of the subject. On the assumption that the root absorbs nutrient ions "osmotically," he estimates from available data on the composition of drainage water, etc., and from considerations of the probable mode of assimilation of nitrogen, phosphorus, and potash in the plant, that the minimal concentrations of these elements in the soil solution, to allow of growth, are nitrogen 2–5 parts per million, PO 1–2 parts per million, K_2O 10–20 parts per million. These values are much lower than those deduced earlier by Rindell[163] from other considerations, and they are only put forward tentatively, recognising that they will vary for different crops, climate, etc. , Emphasis is laid on the need for more work on this question, since before soil analysis can be expected to give results of value, it is necessary to know what the plant's requirements are. When these are known, it will be necessary to find, for any soil, whether it can give the required concentration in the soil solution, and whether it can maintain it.

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[158] *Ibid.*, 1922, **12**, 287; *J.*, 1922, 990A.

[159] *Ibid.*, 1922, **12**, 166; *J.*, 1922, 511A.

[160] *Kolloid-Chem. Beihefte*, 1921, **14**, 63.

[161] *J. Agric. Sci.*, 1921, **11**, 441; *J.*, 1922, 70A.

[162] *Intern. Mitt. Bodenkunde*, 1922, **12**, 11.

The question of absorption and basic exchange in soils, which has an important bearing on soil fertility, and methods of measuring these properties are still attracting much attention. J. Hissink's valuable paper, referred to in last year's report,[164] has now appeared in a German translation,[165] and is thus now more widely available for the detailed perusal it deserves. E. A. Fisher [166] in this country, and A. von Nostitz[167] in Germany have reviewed the present state of knowledge regarding absorption and basic exchange in soils, and the latter has shown how potash starvation may result from the displacement of potash from a soil by basic exchange with ammonium nitrate, followed by leaching.

O. M. Shedd[168] has described an improved method of estimation of total calcium in soils. H. R. Christensen and N. Feilberg[169] have modified Mitscherlich's cobaltinitrite method for the determination of potash in soils, and claim that for small quantities it is now more accurate than the chloroplatinate or perchlorate methods. The use of crucibles of silica instead of platinum for the determination of total potassium in soils by the fusion method has been described by J. S. Jones and J. C. Reeder.[170]

C. Brioux[171] has made a comparison of the Dyer and Schloesing-de Sigmond methods of estimating the "available" potash and phosphate in soils, and concludes that the latter method is better adapted to give an indication of the need for phosphatic manuring, especially with calcareous soils. The determination of sulphates in soil has been studied by C. T. Hirst and J. C. Greaves,[172] who have investigated the sources of error and have compared the gravimetric barium method with the volumetric chromate method. Very small quantities of sulphates can be detected more easily by the latter method. P. Emerson[173] has introduced an improvement in the phenoldisulphonic acid method of determination of nitrates, for soils giving coloured extracts. Collins' calcimeter is often used for the estimation of carbonates and, according to L. A. Sayce and A. Crawford,[174] it is well adapted to this purpose when an accuracy of 0·1–0·2% is sufficient, as it usually is for routine soil work. A. Gehring[175] has described a wet-combustion method for the determination of carbon in soils, which does not appear to differ in any essential feature from the methods commonly in use. In soil analysis it is often assumed that 58% of carbon represents 100% of organic matter. This is, of course, only a rough average figure, of no exact significance; J. W. Read and H. H. Ridgell[176] show that for thirty-seven different American soils the value varies between 30·20 and 56·27, the average being 49·27%.

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[163] *Verhandl. 2ten Agrogeol.-Konferenz, Stockholm*, 1910, p. 103.

[164] See *Ann. Repts.*, 1921, **6**, 415.

[165] *Intern. Mitt. Bodenkunde*, 1922, **12**, 81.

[166] *Trans. Faraday Soc.*, 1922, **17**, 305.

[167] *J. Landw.*, 1922, **70**, 45; *J.*, 1922, 678A. *Mitt. deut. landw. Ges.*, 1921, **36**, 608.

[168] *Kentucky Agr. Expt. Sta. Bull.* 236 (1921); *J.*, 1922, 561R.

[169] *Landw. Vers.-St.*, 1921, **97**, 27.

[170] *Soil Sci.*, 1921, **12**, 419; *J.*, 1922, 25A.

[171] C. Brioux, *Ann. Sci. Agron.*, 1922, **39**, 82.

[172] *Soil Sci.*, 1922, **13**, 231; *J.*, 1922, 511A.

Biological Examination of Soils.

The biological examination of soils, although not strictly coming within the purview of a chemical report, is so intimately connected with the chemical side of soil fertility that a brief treatment of recent work on the subject is not out of place.

A standardised agar medium for counting soil bacteria has been developed at Rothamsted by H. G. Thornton.[177] R. A. Fisher, H. G. Thornton, and W. A. Mackenzie[178] have carried out a critical statistical investigation into the accuracy of the plating method of estimating bacterial numbers, and have found that with Thornton's medium accurate results can be obtained, although excessive variance may sometimes be caused by certain organisms. In the United States, the method of determining the number of micro-organisms in soil tentatively adopted by the Society of American Bacteriologists has been described by S. A. Waksman,[179] who has also discussed the errors in bacterial counts, and their elimination.[180]

The same author has described two media on which soil fungi, but neither bacteria nor actinomycetes, will grow,[181] while H. J. Conn[182] has devised a simple method of demonstrating the presence of fungal mycelium and of actinomycetes filaments in soil. Fragments of mycelium are widely found, though not in great amounts; they are more frequent in soil containing undecomposed organic matter.

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[173] *Soil Sci.*, 1921, **12**, 413; *J.*, 19222, 25A.

[174] *J.*, 1922, 57T.

[175] *Z. anal. Chem.*, 1922, **61**, 273; *J.*, 1922, 641A.

[176] *Soil Sci.*, 1922, **13**, 1; *J.*, 1922, 263A.

[177] *Annals Appl. Biol.*, 1922, **9**, 241.

[178] *Ibid.*, 1922, **9**, 325.

[179] S. A. Waksman and E. B. Fred, *Soil Sci.*, 1922, **14**, 27; *J.*, 1922, 869A.

[180] S. A. Waksman, *ibid.*, 1922, **14**, 81; *J.*, 1922, 869A.

[181] *Ibid.*, 1922, **14**, 153; *J.*, 1922, 949A.

[182] *Ibid.*, 1922, **14**, 149; *J.*, 1922, 950A.

Partial Sterilisation of Soil.

G. Rivière and G. Pichard[183] have obtained 20–50% increases in crops of potatoes, oats, and wheat, from the use of sodium arsenate at the rate of 2–4 grams per square metre (19–36 lb. per acre); a dressing of 95 lb. per acre injured the crop. Their results have been confirmed by R. Ciferri[184] for wheat; this author also obtained similar results with sodium arsenite. From the increased bacterial numbers resulting from the treatment, it appears that the action is at least in part due to partial sterilisation, and not merely to a direct stimulating effect of arsenic.[185] There would, however, appear to be little chance of the practical adoption of this method of partial sterilisation, in view of the risks attendant on the poisonous nature of the agent, and also on account of the possible accumulation of arsenic in the crops produced.

The use of cresol, dichloro-cresol, and other aromatic substances, for partial sterilisation, has been studied.[186]

[183] *Comptes rend.*, 1922, **174**, 493; *J.*, 1922, 225A.

[184] *Coltivatore*, 1922, Nos. 32-34 (Nov. 20 and Dec. 12).

[185] J. Stewart and E. S. Smith, *Soil Sci.*, 1922, **14**, 119; *J.*, 1922, 950A.

[186] T. Parker, A. W. Long, and J. S. Mitchell, *Bull. Bur. Bio-Tech.*, 1922, *No.* 5, 134; *J.*, 1922, 338A.

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SUGARS, STARCHES, AND GUMS.

By James P. Ogilvie, A.I.C.,

Consulting Chemist, 2, St. Dunstan's Hill, London, E.C. 3.

SUGARS.

Statistical.—Probably the most striking feature of the year 1922 in the commercial sugar world has been the way in which consumption has overtaken production. In July, 1920, it was discovered that there was, after all, more sugar in existence than was wanted by the public, and a slump took place in the record prices just previously reached (*viz.*, 23 cents. per lb. for Cuban 96° raws), causing what was perhaps the most serious crisis the industry has ever experienced. For some time after that date, production remained ahead of consumption, with the economic result that sugar was sold at a price unremunerative to the producer, and the industry had to carry on as best it could, with a minimum of expenditure for renewals and repairs. The year 1922 started with little prospect of early improvement. On January 1st the total carry-over of unsold and refiners' stocks (refined sugar basis) was no less than 2 million tons, or roughly 12½% of the world's average consumption then obtaining. Of this amount Cuba was credited with 1¼ million tons, nearly all of which was from her 1920–21 crop; and the prospects of getting rid of this surplus, as well as the new (1921–22) crop, were anything but bright. A prominent New York sugar statistician at that time expressed the opinion that January 1st, 1923, would see a surplus of at least 1¼ million tons.

But these anticipations proved at fault; the demand for sugar all over the world rose unexpectedly, and the huge Cuban stocks were so heavily drawn on that by the end of June all the old crop and two-thirds of the new one was sold. The United States were the principal absorbers. The American *per capita* consumption rose during the first six months of the year to 120 lb. per head, equal to 5,787,000 tons; and for the year ending December 31st last, the consumption of the United States was as much as 5,092,758 tons. The demand for sugared drinks in lieu of alcoholic liquors has certainly had a great deal to do with this augmented consumption, but there is no doubt that the American consumption was bound to rise, given a reasonable price for this article of food. The United Kingdom consumption has also shown a satisfactory increase, having reached 1,604,640 tons for 1922, as compared with 1,338,926 tons for 1921. It would have been higher still but for the fact that there is a stiff duty of 2¾d. per lb. in existence, which virtually doubles the price of the article to the consumer.

The effect of all this absorption of existing stocks is shown by the comparatively small amount of the carry-over on January 1st, 1923 (exact figures not yet to hand). The world's supply of sugar, beet and cane, for 1921–22 is put by Willett and Gray at 17,461,668 long tons. That of 1922–23 will be about the same, preliminary estimates suggesting an increase of 396,000 tons. It is clear then that the production for 1923 is going to be none too much for the demands of the world's consumption, and if the latter increases further, there will be an actual shortage before the 1923–24 crop comes on the market. This shortage would be reflected by a further rise in prices which would stimulate production. Be that so or not, the one satisfactory fact is that the sugar-producing industry has been placed on a remunerative basis once more.

THE CANE SUGAR INDUSTRY.

Extraction of the Juice.—Formerly it was usual to pass the cane directly into the first of the series of three-roller crushing units, constituting the milling installations of the sugar factory; but it is now recognised that in order to realise the highest extraction of the sucrose the hard rind of the cane must previously be reduced to a fine state of division. During the period under review, some attention has been given to appliances for effecting this preparatory treatment, such as crushers and revolving knives. Crushers consisting of two rollers, the surface of which is corrugated or grooved, according to varied designs, so as to split the material into fine pieces, are widely used, and improvements in such "figured" surfaces have been protected by L. G. G. Dibbets,[1] the N. V. de Nederlandsch-Indische Industrie,[2] and by the Machinefabriek Braat.[3] Revolving knives, fixed to a horizontal shaft by some means or other, and rotating in a vertical plane, so as to slice the cane, are now installed in factories in the Territory of Hawaii and the Philippine Islands with successful results, serving the double purpose of disintegrating the stalks, and of levelling the mass of material passing into the two-roller crusher or the three-roller mill, an even feed, and consequently an increased rate of grinding, being thus made possible. Formerly much trouble was experienced in the use of such cutting appliances, owing to frequent breakages, while another hindrance to their more extended application was the difficulty involved in detaching the blades for re-sharpening. Good progress has now been made in overcoming both these disadvantages, and for the mechanical details of such recent improvements the reader is referred to the patent specifications relating to the inventions of A. M. Simpson[4] and C. J. H. Penning,[5] particularly that of the latter, who has provided a strong device from which the blades may conveniently be removed during a stoppage of the mill, so as to permit sharp ones being rapidly substituted in their place. Sometimes the shaft carrying the knives is driven by belt directly from the mill engine fly-wheel, but more usually by an electric motor; and J. L. Renton[6] reports that at Ewa Plantation, T. H., a set of 68 Meinecke blades (a former type) was found capable of cutting 60–80 tons of cane per hour, using a 100 h.p. motor. Regarding the *rôle* of revolving knives in the modern milling installation, as the result of these recent improvements it may be now compared with that played by the shredder.[7] In fact, it is claimed that two sets of about 70 blades each are capable of almost the same performance as the Searby shredder at a very much lower cost and upkeep, and also at a lower expenditure of power. It would therefore appear that this mechanical innovation is well worth the attention of the sugar manufacturer desiring to improve his milling, in respect both of sucrose extraction and crushing capacity.

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[1] Dutch P. 3556.
[2] D.P. 4470.
[3] D.P. 4947.

Having been sub-divided by one or other of these appliances, or by two working in conjunction, such as a shredder and a crusher, or revolving knives and a crusher, the cane passes into the milling plant proper. In order to convey the bagasse or crushed cane from one three-roller unit to the next in the train, steel slat endless belts, and similar types of conveyors have hitherto been usually employed, and have always been found to demand a certain amount of attention; but during the past two years much interest has been aroused by the satisfactory reports[8] of the use of the Meinecke chute.[9] This is simply an enclosed trough rising from one mill at an angle of 35°–45°, and descending to the next at one of 30°–35°, the bagasse issuing from the first mill being pushed up the inclined surface, and falling from the apex regularly and readily towards the succeeding crushing rolls. Entire absence of moving parts, economy of construction, and durability, are the obvious advantages of such a device, compared with the mechanical conveyors at present in use; while its efficiency for installations in which the individual mill units are comparatively close together, has now been decisively demonstrated in a number of factories.[10]

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[4] U.S.P. 1,396,600.

[5] E.P. 182,835.

[6] *Intern. Sugar J.*, 1922, 30.

[7] *Ann. Repts.*, 1920, **5**, 390.

[8] *Intern. Sugar J.*, 1922, 21.

[9] U.S.P. 1,401,095.

In the operation of extracting the sucrose by multiple mills, the crushed fibre retains a greater or less amount of juice, and a point is reached at which pressure fails to expel any more liquid. In modern practice, therefore, a system of applying water to the crushed bagasse, in order to dilute the retained juice, is followed; and in an installation having four three-roller units the procedure may be to spray cold water upon the cane issuing from the third, and to return the weak juice expressed by the fourth to the second unit. Perhaps also the juice from the third might be sent back to the first unit, or other modifications might be adopted; while sometimes hot water is used, the advisability of which has been discussed recently by M. Bird,[11] and by J. N. S. Williams.[12] One of the problems engaging the attention of the sugar factory chemist is to establish the amount of this so-called maceration water which may be profitably employed, since against the increased amount of sucrose extracted by an additional quantity of water must be placed the cost of evaporating it from the juice finally collected. H. Walker[13] has published a contribution to this important question, in which in the particular case of a factory having four three-roller mills he gives calculations and tables showing: the increased extraction which may be realised by increasing amounts of maceration water; the cost of evaporating the increased amount of water added; and the profit or loss that may thus ensue with sugar at different market prices. Such statements of results, though they have a certain general bearing, will, of course, vary greatly according to the nature of the cane ground, and the design of the factory, and will also depend on the circumstance whether it is necessary for the factory to purchase coal or oil to supplement the bagasse used in the furnaces. Nevertheless, the data given by this writer are suggestive, and should prove of value to the chemist when considering the question as it applies to his particular factory.

Clarification of the Juice.—Modern methods of treating the cane as outlined above, involving disintegration and heavy multiple milling, and systematic exhaustion with water, have resulted in a greatly increased extraction of the sucrose, particularly in Hawaii, where, in general, such improvements have been applied to a greater extent than elsewhere. In that progressive sugar-producing country, there are now several factories reporting an extraction of about 99% of the sucrose originally in the cane, and one as high as 99·4%,[14] a figure which demonstrates a really remarkable milling efficiency. But, as has been pointed out in previous reports,[15] this intensive milling has a distinct disadvantage, namely, that the resulting juice is less pure than when by the use of the older installations a more moderate extraction is obtained. Thus, S. S. Peck and others[16] state that, whereas the juice from the first of the three-roller units may have its sucrose, reducing sugars, ash, and " gums " in the proportion of 100 : 12·0 : 1·7 : 0·76, that from the second unit may show the figures 100 : 9·6 : 2·58 : 2·30, and that from the third 100 : 9·6 : 2·61 : 7·82. That is to say, from the first to the second unit the ratio of gums to sucrose has increased 200%, and from the first to the third as much as 900%, which augmentation would have been even much greater had preparatory appliances, as a crusher or a shredder, been included in the milling installation. A large increase in the ash is also shown in these figures. But it is the " gums," or rather the colloidal constituents collectively, that constitute the most undesirable impurities extracted in modern milling, because it is these substances mainly that cause the viscosity of the syrups, from which the sugar is crystallised, thus adversely affecting the yield. Moreover, they contribute to the colour of the juice, the syrup, and the molasses, and, generally speaking, are the source of more or less trouble in boiling, and not infrequently in centrifuging as well.

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[10] *Intern. Sugar J.*, 1922, 22.

[11] *Ibid.*, 1922, 80.

[12] *Ibid.*, 1922, 31.

[13] *Ibid.*, 1922, 183.

Results such as those just cited well serve to demonstrate the great desirability of concentrating on the elaboration of more efficient methods of clarifying the mill juice than are in operation at the present time, methods which shall have as their effect the elimination of most of the colloid impurities that contribute to colour and viscosity, and much of the mineral matter as well. As was mentioned in a previous report,[17] the three processes of clarification, *viz.*, defecation, sulphitation, and carbonatation, which are largely used to-day, are all more or less inadequate as means of efficiently eliminating the colloids, though the best results are given by the latter (in which the greatest quantity of lime is employed). The relative efficiency of these three methods in respect of colloid elimination has been illustrated by

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[14] *Ibid.*, 1922, 32.

[15] *Ann. Repts.*, 1918, **3**, 365 ; 1921, **6**, 420.

[16] *Intern. Sugar J.*, 1922, 140.

[17] *Ann. Repts.*, 1920, **5**, 391.

W. D. Helderman and V. Khainovsky[18] in their study of the colloids which accumulate in the final molasses of Java factories. From their computation of the colloid particles, these investigators obtained figures showing that the number in millions per cub. mm. present in the molasses from factories applying the carbonatation process is only about half that counted in the case of the product from houses employing the ordinary defecation process (in which a minimum quantity of lime is used, just about sufficient to neutralise the natural acidity of the juice).

Recent work carried out in Louisiana, however, points to the fact that, as compared with the use of chemicals such as lime and sulphur dioxide, or lime and carbon dioxide, greatly improved results in respect of colloid elimination are obtained by the application of certain adsorbents. Thus C. J. Gambel[19] states that as small a quantity of decolorising carbon ("Carbrox") as 12 oz. when added to the raw mill juice from 1 ton of cane, will remove a large proportion of the "gums" and about 75% of the colouring matter originally present; while J. F. Brewster and W. G. Raines,[20] acting on the suggestion of F. W. Zerban,[21] have carried out trials in a factory in the same country on the use of kieselguhr, followed by decolorising carbon ("Norit"). These experiments also showed a greatly improved clarification, though unfortunately the cost of the materials in the quantity required to give a sufficient effect appears generally to be such as to render the new procedure uneconomical in competition with the methods in vogue. It would, therefore, seem that one of the most important chemical problems before the industry to-day is the discovery of some means of eliminating the colloidal impurities from cane juice, either by means of an efficient and economical adsorbent, or otherwise.

Efforts are being made also by the engineer to assist in solving the problem of the clarification of the juice by the invention of a filter capable of separating at least some of the gummy matter (after the suspended fine particles of cane, so-called *bagacillo*, have been removed by means of straining through fine gauze). It should be premised that the filtration of the raw juice through plate-and-frame presses, or similar apparatus, is in practice impossible, owing to the rapid formation of an impenetrable layer of slime over the surface of the cloths. It follows, therefore, that the problem is a particularly difficult one, so that it is of much interest to observe the way in which it has been approached by two inventors. W. Mauss[22] has described a vacuum filter for the treatment of raw juice, which consists (as Fig. 1 shows) of two compartments, *viz*,

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[18] *Intern. Sugar J.*, 1922, 89; *J.*, 1922, 226A.
[19] *La. Planter*, 1922, 69, 141.
[20] *Intern. Sugar J.*, 1922, 605.
[21] *Ibid.*, 1920, 332, 643, 699; *J.*, 1921, 21A.
[22] E.P. 176,395, 177,067, 181,123; *J.*, 1922, 315A, 358A, 576A

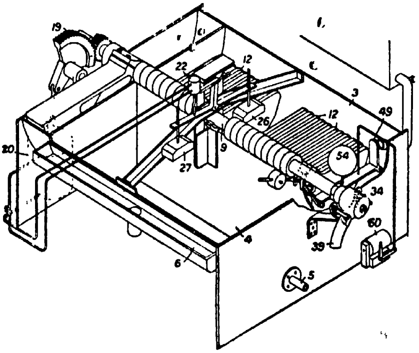

FIG. 1.

the filtering tank, 3, and the cleaning tank, 4. A series of leaves, 12 (dressed with cloth), is supported by a hollow shaft, 9, capable of oscillation. As the leaves in the tank, 3, become clogged, the supply of unfiltered liquid is gradually decreased, being entirely shut off when the outflow has fallen to a pre-determined limit, at which point a motor oscillates the shaft, 9, causing the leaves to swing over into the cleaning tank, 4, where the colloidal deposit is detached from the filtering surface by a thin continuous sheet of water, impinging at a slight inclination to the surface of the leaf at a very high velocity, the leaf and the nozzle supplying the sheet of water being moved relatively past one another.[23] Steam may also be admitted to the interior of the leaves. This cleansing operation accomplished, the leaves are swung back into the liquid in the filtering tank, 3, suction is resumed, and filtration is continued. It is thus seen that during most of the time in which filtration is actually taking place, the liquid will be passing through a thin layer of colloid matter on the surface of the cloths, so that, in addition to fine particles of bagasse and other solid matter, a certain proportion of the colloids of the raw juice (though probably not a high one) should be eliminated in this way. The second inventor, R. Vachier,[24] also uses a filter leaf, but operates it under pressure, the plates being made of wire cloth, while a means of removing by scrapers the layer of colloid matter when it has reached

[23] E.P. 181,123; *J.*, 1922, 576A.
[24] *Intern. Sugar J.*, 1922, 211, 270, 664.

a certain thickness (about ¼ in.) is provided. This filter is reported to have been successfully operated in two sugar factories, one in Louisiana and the other in Porto Rico, though details of the results claimed have not yet appeared in print. Other inventors, such as L. J. Martel,[25] are attacking the difficult problem of the filtration of the entire juice from the mill; but in passing it may be observed that no one seems yet to have studied the application of Plauson's colloid filter to raw cane juice, and a trial in this direction surely appears well worth making.

An alternative procedure to filtration through cloth or other medium is treatment in some type of machine, in which by means of centrifugal force the solids are thrown to the periphery of an imperforate drum, while the clear liquor in the central portion is discharged in some convenient manner. Many attempts have already been made in the cane sugar industry to utilise this principle in the case of raw or limed juices; but hitherto, owing to a variety of reasons, largely to the slimy nature of the substance separated, success does not yet appear to be won. It is, however, now possible to record some progress made in this direction. Using a continuously operating machine of a novel and attractive design, invented also by W. Mauss[26] (for the mechanical details of which the reader is referred to the patent specification), W. A. Caldecott[27] found in a factory in Natal, that 96·6% of the solids and *bagacillo* originally present could by this means be eliminated rapidly and conveniently. This is of course a considerably better result than would be obtained by any system of screening, and means the production of a juice which can be much more easily and completely clarified by the defecation, sulphitation, or carbonatation method than ordinarily. It would now be of interest to read of trials made with this machine for the purpose of treating the juice after it has been limed. A system as this of removing the insoluble matter from the raw or limed juice by centrifugal force would greatly facilitate the task of clarification, especially if continuous; and, if truly practicable, would constitute one of the most important advances possible in the science of sugar manufacture.

Certain of the other stages involved in clarification are probably susceptible of some improvement so far as mechanical details are concerned. Once again W. Mauss[28] has applied his ingenuity, and has in fact elaborated a scheme for the operation of the sulphitation process almost automatically throughout. Juice from the mill, 1

[25] *Ibid.*, 1921, 641.
[26] E.P. 164,418; *J.*, 1921, 535A.
[27] *Intern. Sugar J.*, 1922, 308.
[28] E.P. 182,855; *J.*, 1922, 777A.

(see Fig. 2), passes successively to a continuous sulphuring appar-

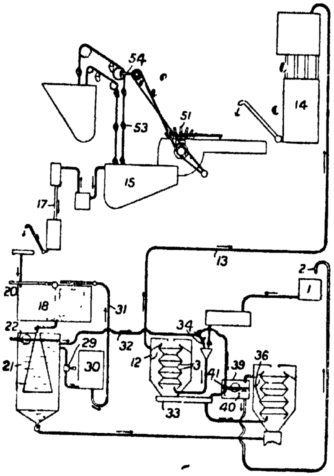

FIG. 2.

atus, 14; the water-wheel, 51; the liming tank, 15; the heater, 17[29]; the filter, 18[30]; and lastly, the pipe 20, which conveys the resulting clarified juice to the evaporators. Water is supplied from the tank, 21, for washing the insoluble matter in the filter, 18, and the centrifugal, 3, while the separated solids from the latter machine are discharged into the tank, 33, and rewashed in the centrifugal machine, 36, the liquid from which is used for the maceration or exhaustion of the cane undergoing crushing in the mills. Those knowing the refractory nature of the juice of the Uba cane, with which this engineer is working, will probably agree that this scheme is an ambitious one. Nevertheless, results of its operation will be watched with a good deal of attention by all, and especially by those clarifying juices more amenable to treatment than those extracted in Natal.

Lastly, under the heading of the clarification of cane juice it may be mentioned briefly that the Petree process described in a previous report,[31] has now been installed in a number of factories in different parts of the world[32]; that P. A. Bour[33] has again called attention to the importance of using lime of good quality for clarification; and that E. Wuthrich[34] has reported excellent results with the use of the carbonatation process in Natal.

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[29] E.P. 173,709; *J.*, 1922, 163A.

[30] E.P. 176,395; *J.*, 1922, 315A; E.P. 181,123; *J.*, 1922, 576A.

[31] *Ann. Repts.*, 1919, **4**, 379.

[32] *Intern. Sugar J.*, 1922, 621.

[33] *Ibid.*, 1922, 493.

Evaporation of the Juice.—After having been clarified, the juice containing 12–18% of total solids is concentrated in a triple or quadruple effect evaporator to a syrup of 50–60% (50°–60° Brix). Previous to evaporation, it is more or less clear, depending on the method of clarification which has been applied; but as the water is eliminated certain inorganic impurities, which were soluble in the dilute liquid, gradually separate out. Part of these deposit on the heating surfaces of the evaporator; while the rest remains in suspension, later to be allowed to precipitate in the syrup storage tanks, or sometimes to be separated by filtration. Since even a thin deposit of scale inhibits heat transmission to a marked degree, a good deal of attention has always been directed by investigators to the cause of its formation. It has been established that its composition varies according to the particular vessel of the multiple effect evaporator from which it is detached. Present opinion on the matter is that the formation of an incrustation on the heating tubes must be regarded as inevitable, though capable of control to a certain extent by the use of lime of high purity, as has again been emphasised by E. Wuthrich,[35] and of course also by working with juice which has been freed from suspended matter by careful clarification.

Although the incrustations resulting from the evaporation of juice clarified by the defecation, sulphitation, or carbonatation process have been closely studied, hitherto the opportunity has never arisen for the examination of the precipitate thrown out of solution after treatment with the method of purification involving the use of decolorising carbon. J. F. Brewster and W. G. Raines,[36] when applying this new mode of working, have observed that no matter how brilliant the juice may have been before evaporation, a certain amount of precipitate containing a high proportion of silica invariably appears when its concentration has reached a certain degree. This was an unexpected result, as heretofore it has been taken for granted that the constituents of the deposit were mainly derived from the chemicals used in the particular process of clarification adopted. In the case of clarification with decolorising carbon ("Norit") alone, this could hardly be so, because only about 1% of this preparation was added, and its total ash content does not exceed 6–7% as a rule (before revivification). V. Birckner[37] had previously made the same observation, and in order to prove that the constituents of the scale were not derived from either the decolorising carbon or the kieselguhr, which had been used in conjunction in his experiments, these materials were extracted repeatedly with an artificial cane juice. A negative result was obtained; and this chemist consequently expressed the opinion that the formation of the precipitate is to be attributed mainly to "factors inherent in the juice itself."

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[34] *Ibid.*, 1922, 246.

[35] *Ibid.*, 1922, 493.

[36] *Ibid.*, 1922, 605.

[37] *La. Planter*, 1922, **68**, 285.

A more definite explanation has, however, been reached by J. F. Brewster and W. G. Raines,[38] who, using juice milled from washed and unwashed cane, obtained significant results. Juice from cane from which all mud and earth had been carefully removed previous to milling gave precipitates which contained appreciably less mineral matter than ordinarily, leading these authors to the belief that the formation of a deposit during evaporation is to be attributed quite largely to the introduction of colloid substances from the dirt adhering to the cane, though also in part to substances present in the juice itself, and to some extent also to the chemicals added when the defecation or sulphitation methods of clarification are applied.

Yet another useful contribution to our knowledge of this irregularity is made by M. Bird,[39] as the result of work done in factories in British Guiana. This investigator noticed the high proportion of silica present in the precipitate separating from syrup in the evaporators, an observation which led him to turn to the statement made by C. Müller,[40] that cane juice contains organo-silicious compounds in the colloidal state, capable of being destroyed by heating to about 248° F. (120° C.). Bird has put this idea into practical effect by preliminarily raising the temperature of the raw juice as high as was possible in the tubular heaters at his disposal, *viz.*, to 220° F. (104° C.), when a precipitate presumably containing a large amount of silica resulted, and was separated by straining through 100-mesh gauze. Subsequently clarification was carried out in the usual way, but it was found that only a third to a half of the quantity of lime ordinarily required to produce the usual effect in clarification was necessary. A sufficient amount of sugar (about 2000 tons) was made by this procedure to prove to the mind of its originator that it had exercised a marked influence on the quality and also on the yield of the product, the result finally being a molasses which in purity was several degrees lower than had ever been obtained in the particular factory in which the modification has been instituted. This method of working, therefore, appears promising. Now and again the observation has been made in different countries that the amount of incrustation seems to vary,

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[38] *J. Ind. Eng. Chem.*, 1922, **14**, 946; *J.*, 1922, 950A.

[39] *La. Planter*, 1922, **69**, 61.

[40] *Intern. Sugar J.*, 1921, 579; *J.*, 1921, 402A.

ceteris paribus, according to the variety of cane ground; so in factories where this may be the case it would probably be worth while pursuing Müller's suggestion further by carrying out determinations of the silica content of the stalks, of the raw juice extracted, and of the juice after heating to a high temperature.

Although the adoption of Bird's modification may be expected to result in an appreciable diminution in the amount of scale, yet its formation can hardly be obviated entirely, since other constituents than silica enter into its composition. Means for its removal will still have to be considered; and at the present time treatment with sodium carbonate or sodium hydroxide (a solution containing about 2%), followed by hydrochloric acid (1%) is very generally used. J. W. Donald[41] now makes the statement resulting from his experience in factories in the Territory of Hawaii, that a hard incrustation may be converted to a slime by allowing it to stand during 1-5 days in contact with a comparatively strong solution of caustic soda (13-25%), the usual treatment with hydrochloric acid being then unnecessary; while H. S. Walker[42] says that he has obtained good results by boiling out the evaporator for half-an-hour at atmospheric pressure with caustic soda (10%), emptying, turning on steam for half-an-hour, boiling out with water, and finally with dilute acid. On the other hand, there are technologists who assert that such chemical methods are inferior in respect of cost, speed, and efficiency to mechanical means; and, whether this view be generally accepted or not, it may be noted that the scraper invented by H. W. Taylor[43] is reported to be giving very good results in South Africa, Mauritius, and Demarara.

Boiling to grain, and finishing.—In making raw sugar which subsequently is to be refined, the syrup emerging from the multiple effect evaporator seldom undergoes any treatment for the elimination of the precipitate which has formed during its concentration other than being allowed to stand in the vacuum supply tanks (often, it may be added, for an insufficiently long time). Usually the syrup is too dense for a satisfactory subsidence, and a more efficient and convenient treatment is greatly to be desired at this stage, since trouble in crystallisation, and later in separating the grain in the centrifugals, is sometimes to be traced to the presence of suspended solids. On the other hand, in white sugar manufacture the use of a perfectly brilliant syrup for crystallisation is an absolute *sine quâ non*, if a product of the highest grade for direct consumption is the object in view; and the means of realising this at the present time is by filtration through bag, leaf, or plate-and-frame presses. Here again the importance of the elimination of the colloids is seen, for unless clarification has been sufficiently thorough to get rid of most of the "gums" (as, for example, when the carbonatation process has been applied) filtration at this stage is a comparatively troublesome and slow operation, and indeed often an impossible one. It follows, therefore, if the defecation or sulphitation methods have been used for the treatment of the juice, that in order to make filtration possible at this stage some process of clarifying the syrup (and of thus eliminating a further proportion of the colloids) must be applied. Perhaps the most convenient, efficient, and economical procedure which we have at present for this purpose is that known as Bach's process, to which allusion was made in a previous report.[44] Milk of lime at 15° Bé. (in the amount of 2–3% by vol.) is run into the cold liquor and sulphur dioxide passed in at the same time, the reaction adjusted to neutrality to phenolphthalein, and the temperature raised nearly to boiling point. Filtration through cloth in plate-and-frame presses follows, the result being a brilliant and light-coloured syrup, from which a good white sugar can ultimately be obtained. B. Block[45] has pointed out that in the application of this sulphitation process the calcium sulphite is precipitated from syrups of 55° Brix and 88°–89° purity in the form of spherical crystals of only about 1 μ; whereas when the same method of simultaneous liming and sulphiting is performed with juice at about 15° Brix, the crystals are larger, namely about 3–4 μ. There is a quantity of plantation white sugar imported into this country which unfortunately just falls short of the necessary appearance demanded by the grocery trade, and in consequence realises a lower price than might otherwise be the case. Its principal defect is the presence in it of a comparatively high amount of insoluble matter, entrained during crystallisation from an unfiltered syrup; and the attention of the manufacturer of such grades is directed to the advantages of Bach's process. It is economical in operation, no special plant other than a sulphur oven and some additional tanks being required; the routine is reasonably simple, demanding but little extra supervision; while further the cake of calcium sulphite which is obtained in the presses can be washed down to a low sucrose content quite readily. Altogether, therefore, this seems a practical process, one which is worthy of close consideration by all concerned with the problem of syrup filtration.

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[41] *Ibid.*, 1922, 638.

[42] *Ibid.*, 1922, 640.

[43] E.P. 127,737, 160,362.

Returning to raw sugar production, it may again be pointed out[46] that the method of taking off successive crops of crystals from the syrup, the first and second mother-liquors, and perhaps also the third, is being practised less and less. It is wasteful of time, labour, and steam; and another consideration is the difficulty of marketing the impure last crops of crystals, that is, sugars polarising only 85–90%. Now-a-days the system of "boiling-in" the first and second mother-liquors with the purer syrup coming directly from the evaporators, followed by so-called crystallisation-in-motion for the exhaustion of the last molasses, is very largely adopted.

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[44] *Ann. Repts.*, 1919, **4**, 389; and U.S.P. 1,104,095; *J.*, 1914, **935**.

[45] *Deuts. Zuckerind.*, 1922, **47**, 443.

[46] *Ann. Repts.*, 1919, **4**, 382.

There are numerous modifications of this "boiling-in" system in operation, and the choice of any particular one is controlled by a number of conditions, two of the most important of which are the initial purity of the syrup, and the arrangement and capacity of the existing plant of the factory. H. S. Walker[47] has suggested that it would be desirable that a standard system should be adopted by the factories in Hawaii, and a careful consideration of the methods in vogue elsewhere has led him to suggest one in which the process of de-saccharification is performed in three stages, namely: (*a*) with evaporator syrup and low-grade sugar (from the last molasses), the grain formed being built up by the addition of further syrup, and also some liquor obtained by the re-melting of low-grade sugar, but without the use of any molasses, (*b*) with syrup and low-grade sugar as previously, but finishing by drawing in all the molasses resulting from the centrifuging of the magma (or massecuite, as it is called) obtained at the end of stage (*a*); and (*c*), again starting with syrup and low-grade sugar, and finishing by drawing in all the molasses from stage (*b*). Lastly, all the molasses from stage (*c*) is boiled to grain, and discharged into the crystallisers-in-motion, where, while being slowly cooled and gently agitated, a further deposition of sugar on the existing crystals is effected, and the molasses finally exhausted as far as is possible with the methods of clarification at present in use.

On the whole, this system of boiling appears to have been favourably received. Thus A. Fries[48] states that he has already used one essentially similar with satisfactory results, finding it to be economical in respect of labour and steam, and, further, to possess the advantage that (contrary to certain other systems) the re-boiling of molasses is brought to a minimum. H. D. Beveridge, R. J. Richmond, and others[49] have also commented upon it appreciatively. In general, the method would appear to offer several distinct advantages over that now largely used in the Territory, in which syrup and molasses are boiled together in such proportions as to give a first massecuite of one purity ratio, *viz.*, 76°–78°, the criticism against such a procedure being that more molasses is kept in circulation, and in consequence, the boiling mass is more viscous, the yield of sugar is lower, and the vacuum pan capacity required is greater than would otherwise be the case. On the other hand, a possible objection to Walker's proposal that immediately occurs is that three grades of sugar are made, whereas a raw sugar polarising about 96% is the product demanded by the buyers, *viz.*, the refiners in the United States. However, this obstacle to its adoption does not really exist, since it is easy to adjust conditions so that the polarisation of the three grades does not vary beyond the extremes of 95 and 97%, as experience with the process in making a large quantity of raw sugar has proved.

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[47] *Intern. Sugar J.*, 1922, 637.
[48] *Ibid.*
[49] *Ibid.*

Turning to the technique of the actual operation of boiling the content of the vacuum pan to grain, it is of not a little interest to note that a number of managers in the Territory of Hawaii are employing the method of "seeding" the supersaturated solution by drawing in white powdered sugar, an innovation which was recorded in a previous Report.[50] Thus G. Giacometti,[51] using about 1 lb. of the fine crystals per 1000 cub. ft. of liquor in the pan, found that the resulting grain formed is certainly more uniform, and also appears more readily, than ordinarily; while R. C. Pitcairn[52] obtained improved results from the application of this method to low-grade massecuites, sugars being thus produced which are more easily "cured" in the centrifugal machines. Incidentally, it may be remarked that the same method is in use at the Crockett Refinery, Cal., U.S.A., and also at the Oxnard beet factory, as is stated elsewhere in this Report.

Coming to the final stage in the manufacture of sugar in the cane factory, namely, the centrifuging of the massecuite (or mixture of crystals and molasses), after it has been dropped out of the vacuum pans or crystallisers-in-motion, there is nothing in particular to record under this reading from the point of view of applied chemistry, though mention should surely be made of three patented mechanical devices, each of which appears of importance. The first refers to an apparatus for continuously centrifuging by J. Avrutik[53]; the second to a device for washing the crystals in the centrifugals by R. A. Steps[54]; and the third to an apparatus for effecting the discharge of the contents of the basket of the centrifugal after "spinning" has been completed, the invention of A. R. Robertson and A. F. Dunsmore.[55]

THE BEET SUGAR INDUSTRY.

Before commencing the technical survey of this branch of our industry, it is relevant to remark that the British beet sugar ventures, Cantley and Kelham, have received an unexpected fillip in the form of a remission of the excise duty, which in effect amounts to a bounty of some £24 per ton of sugar produced. Kelham factory, the installation of which was recently described,[56] was conceived and erected at a period when prices for constructional work were at a peak, and in consequence was greatly over-capitalised for a concern of its contemplated output. Its 1921-22 season resulted in a heavy loss, and various difficulties, financial and otherwise, threatened to close it altogether. As the Government had sunk a good sum of money in the venture, they had to decide whether to cut their losses or assist the undertaking further. They chose the latter course, and remitted the excise duty on this home-grown sugar *sine die*, on the grounds that it was an agricultural experiment of value to the country, which should have a fair and prolonged trial. This financial aid came too late to enable Kelham factory to operate during the 1922-23 "campaign"; but to keep the beet sugar interest alive in its neighbourhood a working arrangement was come to between the two factories by which last autumn the whole of the roots from both areas were to be worked up at Cantley, which is in a good running condition. It is estimated that the total quantity of roots sliced during the 1922-23 season just completed was about 54,000 tons; and assuming an average price of 38s. per ton for these delivered at the works, an average extraction in the form of white granulated sugar of 12%, a cost of manufacture of about £12 per ton of finished sugar, and an average price for the product of £48 per ton, it may be concluded that this business must now be a very profitable one, so long, of course, as the remission of the duty is continued.

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[50] *Ann.-Repts.*, 1919, **4**, 383.

[51] *Intern. Sugar J.*, 1922, 638.

[52] *Ibid.*

[53] E.P. 176,446; *J.*, 1922, 317A.

[54] U.S.P. 1,423,583.

[55] E.P. 172,862, 178,380; *J.*, 1922, 88A, 401A.

Extraction of the Juice.—At the present day, in almost every factory in the world, sugar is extracted from the beetroot (after it has been "sliced") by means of a diffusion battery of 10-14 lixiviating vessels. Many have been the attempts that have been made since Robert installed the first diffusion battery in 1864, to carry out the operation in a single vessel continuously, but none has hitherto found any extended use in the industry. Almost in every case these efforts have failed to comply with two conditions, which are essential to any process for the extraction of the juice from the beet, namely: (1) the production of a juice of a sufficiently high gravity; and (2) the complete and even exhaustion of the so-called "slices" or cossettes. Undoubtedly the problem is a difficult one; but its solution might have several very important advantages, such, for example, as the formation of a denser juice than is obtainable at the present day by means of the diffusion battery (thus reducing somewhat the coal bill of the factory); automatic action; and economical construction. Another advantage that might accrue is the avoidance of waste water (both from the battery and from the slice presses), which constitutes one of the defects of the present method of working.

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[56] *J.*, 1922, 149R.

It is, of course, easy to imagine that the problem could be solved by so arranging matters that the juice in a steady stream should meet the beet slices coming in the opposite direction, but the mechanical difficulties that arise in endeavouring to put this idea into effect are many. These principally involve the upward or downward movement of the slices without the formation of a compact, impenetrable mass; the regular circulation of the juice throughout the whole of the beetroot; and the maintenance of the lixiviating liquid at a sufficiently high temperature.

It is possible now to record three developments in the conduct of continuous diffusion. Sir J. I. Thornycroft[57] has devised a method possessing great possibilities, in which provision appears to have been made for the avoidance of the principal difficulties that have been proved to arise when attempting to effect diffusion in a single vessel. His construction provides a vertical column, up which the sliced material is forced by means of a screw against a descending stream of water, which screw may be interrupted or continuous, and either perforated or not, and is rotated intermittingly by means of one or more hydraulic rams acting through a ratchet gear. In order to cause the circulation of the liquid in the diffuser, transverse pipes and pumps are bolted on the sides of the tower, so as to withdraw juice, circulate it through external pipes, and return it to a point diametrically opposite to that from which it was taken; while the necessary temperature is maintained by introducing steam jets into these pipes. Publication of particulars relating to this apparatus has aroused some attention on the Continent, and arrangements have been made for its trial on the factory scale. Experiments made in this country in a small apparatus have shown the concentration of the juice to be 14·7° Brix, and the sucrose content of the exhausted wet slices to be 0·2%, figures which would seem to indicate a satisfactory operation of the process so far as one can judge from an analysis of the products concerned.

Some years ago Hyross and Rák, in place of a single cell, constructed a more complicated plant, involving a combination of diffusion and pressure, and a certain degree of success resulted from their efforts. Recently improvements of the original apparatus have been protected by the last-named inventor.[58] *A* shows the construction of the diffusion vessel, and *C* that of the slice press, several of these two elements being connected together in series, by means of horizontal conveying troughs. Sliced beet is fed to the top of the vessel, *A*, passed down through an ascending column of liquid, and is discharged from the bottom by rotary blades, *b*, *e* (and by other blades acting therewith, not here shown), through the horizontal conveying trough to the press, *C*, from the top of which it is dropped by way of the shoot, *h*, into the next diffusion vessel of the series. Water (or weak juice from a previous member of

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[57] E.P. 120,448, 166,993; *J.*, 1919, 49A; 1921, 711A.

[58] E.P. 166,527; *J.*, 1922, 777A.

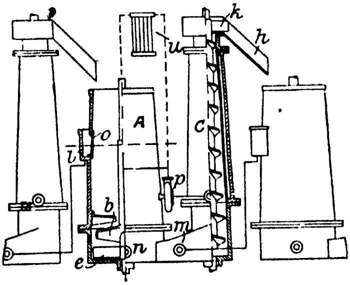

FIG. 3.

the series) enters the system at *m*, and liquid which has been forced out of the slices by the press is withdrawn at a point opposite the pump, *p*, by which it is forced through a heater, *u*, into the diffusion vessel at *n*. Juice overflows from the diffusion vessel through a strainer, *o*, and a gutter, *l*, passing into the following press at the point, *m*, or (in the case of the last member of the series) leaving the extraction apparatus for the following stage in the process of manufacture, *viz.*, clarification. It will thus be seen that this apparatus has the great advantage of being continuous, and apparently almost automatic; of obviating entirely the formation of waste waters; of being capable of producing a juice of high density; and lastly of providing pressed exhausted slices, suitable for cattle food. On the other hand, on comparing it with ordinary diffusion, it occurs to one that the mechanism for the repeated pressing of the slices must involve a certain expenditure of power; while the cost of the whole apparatus would probably be at least as great as that of a 14-vessel diffusion plant. Whether these possible disadvantages may be counterbalanced or outweighed by the benefits mentioned does not appear yet to have been conclusively decided by large-scale practice.

Attention must also be directed to a third invention for the continuous extraction of juice from the beet, namely that protected by the S.A. des Établissements A. Olier.[59] It consists of an enclosed series of vertical columns up and down which the beet slices under treatment are carried in counter-current to the extraction liquid by means of an endless conveyor, provided with perforated plates carried on endless cables, the several columns being jacketed for the circulation of steam or hot water, in order to maintain a sufficiently high temperature during the operation of extraction. In regard to this apparatus, it is claimed that its cost would be less than that of an ordinary diffusion battery of the same capacity; that juice at about the same density as that usually obtained in a battery would be drawn off; and further, that the lixiviated material discharged would be entirely exhausted, an important advantage, since the sugar content of the extracted pulp in the practice of to-day may be about 0·5%. On the whole, therefore, the proposed method of working appears an attractive one. It will certainly be of interest to see whether trials on the technical scale are capable of corroborating the claims just mentioned, though the most important of all (which has yet to be established) is whether by means of the mechanical arrangement described all the pulp will be held by the plates during their long travel up and down the closed conduits; or whether, on the other hand, a quantity of fine material will not largely be carried away with the juice withdrawn from the process. If the mode of effecting counter-current extraction specified in this patent proves to be practicable, this invention should certainly form an important improvement in the operation of continuous beet juice extraction.

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[59] F.P. 539,104.

Clarification of the Juice.—In standard practice, liming is carried on at about 75°–80° C., and may last 10–15 min., at the end of which time the treated juice is sent to the so-called saturation tanks, in which carbonating is carried out. A great number of chemists at different times have advanced the opinion that during the process of liming certain of the precipitated non-sugars again pass into solution, forming strongly melassigenic impurities. In consequence they have advocated the performance of this part of the process of clarification according to the following stages: (*a*) treatment of the heated raw juice with a small quantity of lime, just about sufficient to produce the chemical effect only; (*b*) separation of the precipitate thus formed; and (*c*) addition of a further larger amount of lime. It is claimed that by operating in this way not only is the formation of harmful hydrolytic protein products avoided, but also the total amount of lime required is less than that ordinarily necessary. Many modifications of this procedure, and methods of putting it into practice, have been proposed, and in a previous Report[60] allusion was made to two of the most important of these, *viz.*, those elaborated by E. Kuthe and E. Anders,[61] and by K. Kowalski and S. Kozakowski.[62]

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[60] *Ann. Repts.*, 1920, **5**, 407.

[61] G.P. 50,032.

[62] G.P. 138,693.

It is now possible to examine further this question on three grounds, namely: (1) its necessity; (2) its economy; and (3) its practicability. V. Stanek,[63] as the results of experiments, particulars of which it is unnecessary to reproduce here, found it to be true that under the conditions obtaining in practice a 'comparatively considerable amount of the precipitate does again pass into solution, namely about 12% after about 15 min. at a temperature of 85° C., thus confirming the belief of the earlier workers. This addition to the soluble impurities appears mainly to be caused by the alkaline hydrolysis of the coagulated proteins, it being possible to detect albumoses, peptones, and polypeptides in the resulting liquid, though not amino-acids. At the same time, however, the important observation was made that, although a portion of the precipitate was thus rendered soluble, yet after carbonating (provided a sufficient amount of lime had previously been added) the purity ratio of the juice obtained after filtration is not much lower than when the precaution was taken to remove the lime precipitate. This may appear remarkable; but the explanation would seem to be that the impurities passing into solution as the result of the action of the lime, as well as certain constituents of the juice, such as soluble calcium salts, are adsorbed by the precipitate of calcium carbonate during its formation in the saturation tanks. This interpretation finds confirmation in the fact that from filter-press cake (after it has been washed with water for the extraction of the sugar retained) it is possible to separate a number of soluble impurities. Hence, once more the so-called physical effect of the clarifying operation is demonstrated.[64] As, even under the most disadvantageous conditions of liming, the lowering of the purity ratio amounted in these experiments to only 0·16°, and averaged 0·10°, it may certainly be concluded from these results that, judged from the point of view of the purifying effect, the modification under discussion is indeed an unnecessary one.

Regarding its possible economy in respect of lime, V. Stanek and J. Vondrak[65] have gone carefully into this matter, and in a series of comparative laboratory tests carried out under varying conditions they obtained results showing clearly that if the total amount of lime added is much less than 2% the clarification is incomplete. Their nett conclusion was that it is not possible to economise in lime by the preliminary removal of the precipitate resulting from the addition of a small quantity of this reagent, in the manner explained. This decision appears to support the belief expressed by A. Herzfeld[66] that the precipitate resulting during liming in combination with the excess of lime in suspension forms an adsorbent possessing a considerable clarifying effect; while it may be recalled that H. Claassen[67] has insisted that all these modifications in which less than the usual amount of lime is employed invariably lead to the production of insufficiently purified juices, holding much lime in solution, and causing trouble in the last stages of sugar exhaustion.

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[63] *Z. Zuckerind. Czechoslov.*, 1922, **46**, 663, 671; *J.*, 1922, 870A.

[64] *Ann. Repts.*, 1920, **5**, 406.

[65] *Z. Zuckerind. Czechoslov.*, 1922, **46**, 299; *J.*, 1922, 385A.

[66] *Deuts. Zuckerind.*, 1920, **45**. 244.

Assuming for a moment that such processes are really advantageous, and that, as Z. Vytopil[68] and others declare, the preliminary precipitate may find some use as a nitrogenous addition to fodder—neither of which suppositions appears to be founded—there remains the question of the practicability of the procedure. J. Prochazka[69] mentions the difficulty of filtering beet juice treated with a small amount of lime, owing to the slimy nature of the precipitate. Attempts have been made to obtain a comparatively clear liquid by subsiding, leaving only a fraction of it to be filtered; but the results reported along this line by V. Skola[70] do not impress one as encouraging, it being often impossible to obtain a clear liquid, even after standing for a comparatively long time. Hence, summarising the work which has been reviewed above, the final conclusion to be drawn is that the proposed deviation from the customary method of operating clarification is unnecessary, uneconomical, and impracticable.

Evaporation of the Juice.—Although the concentration of the clarified juice from a density of 13°–16° Brix to one of about 60° is a physical process, yet during its progress certain chemical reactions may occur, and one of these, *viz.*, the retrogression of the alkalinity imparted to the juice during the last stages of clarification, is of much importance.

Diminution of the alkalinity during evaporation is caused by the hydrolysis in the alkaline medium of the proteins and derived proteins present in the juice, and it may even proceed so far that the reaction becomes an acid one, the serious danger of loss of sucrose by inversion thus being incurred. Normally the alkaline hydrolysis is almost completed during liming and carbonating; but after an unusually dry summer the protein content of the beet may be so high that this reaction is only partially effected during the operations mentioned, leaving it to be continued in the evaporator to the disturbance of the usual course of events. It is the amides, asparagine and glutamine, that are principally concerned in the phenomenon under discussion, the corresponding amino-acids being formed, and ammonia volatilised. With the object of learning something more of the conditions under which this decomposition may proceed in the beet factory, J. Vondrak[71] has studied the behaviour of various amides when heated in aqueous solution with lime. Glutamine, he found, was readily transformed, asparagine less readily, and choline and allantoin quite inappreciably. A point of practical importance which was observed is that a more intense decomposition results when lime is added in the cold to the amide solution, which is then heated, than when it is added to the heated solution ; and as an advantageous procedure it was suggested that in the factory the lime should be added to the cold juice, which subsequently should be heated and carbonated, so as to ensure that the amount of decomposition during concentration may be reduced to the minimum possible. Further, for the same reason it was mentioned as advisable that some lime should be added before the second carbonatation, and that the subsequent saturation with carbon dioxide should be operated at 100° C. These recommendations appear well founded, and if put into practice may do much to alleviate one of the irregularities which, at times, demands the close attention of the beet factory chemist.

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[67] *Deuts. Zuckerind.*, 1918, **43**, 191; 1919, **44**, 57, 359.

[68] *Z. Zuckerind. Czechoslov.*, 1922, **46**, 236; *J.*, 1922, 226A.

[69] *Ibid.*, 1922, **45**, 306.

[70] *Ibid.*, 1922, **46**, 601, 625; *J.*, 1922, 775A.

Boiling to Grain and Finishing.—Excepting when (as just stated) there has occurred an abnormal decrease of the alkalinity during concentration, the syrup from the evaporators requires to be carbonated or sulphited in order to reduce its reaction almost to neutrality before it enters the vacuum pan to be boiled to grain. It is then generally filtered, though according to B. Bartsch[72] some raw sugar manufacturers in Germany appear lately to be inclined to omit this operation, presumably assuming the view that it is an unnecessary one, seeing that the product has anyway to be refined. If this tendency were carried into effect generally, it would be a retrogression, for there is no doubt that a purer raw sugar, having usually a better grain, and generally much easier to treat in the refinery, is obtained when the syrup before being drawn into the pan is carefully filtered. Several types of apparatus may be used for this purpose, and two have recently been patented. The first is a sand filter by L. E. Raimbert,[73] and the second a rotary disc appliance by H. A. Vallez,[74] the latter being stated by W. D. Horne[75] to have given satisfactory results in America, in respect of rapidity of discharging, cleaning, re-filling, and thoroughness of washing.

In the process of boiling the syrup to grain in the vacuum pan, the purpose which is kept in view is to form in the thickened liquor the necessary number of crystals, these only then being allowed to grow by further concentration. Care is taken throughout the operation to guard against the formation of a perceptible amount of new ones, since the presence of "fine grain" or fine meal in the finished product (termed massecuite) makes the subsequent separation of the crystals and molasses in the centrifugals difficult, and indeed at times impossible. At the Oxnard factory, California, where boiling is carried out with great rapidity, it has been found of great assistance in securing regularity of grain to draw into the pan a small amount of white sugar, when its contents have reached a state of supersaturation, and just at the moment when the grain is about to appear. It is said by A. Vasseux[76] that this addition not only enables boiling to be performed quickly, but in addition obviates the formation of the dreaded "false grain," gives a sugar of better colour, and improves the extraction. This device for effecting "seeding" is reported to have been adopted also at the Crockett Refinery, California, and in some Hawaiian factories (as has been mentioned already), and generally the claim regarding the formation of a more uniform grain has been supported, though the other statements just mentioned have not yet been verified. It is certain to be put on trial in other factories in different countries, and reports on its value will be read with not a little interest.

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[71] *Ibid.*, 1922, **46**, 483, 533, 589 ; *J.*, 1922, 776A.

[72] *Deuts. Zuckerind.*, 1922, **47**, 443.

[73] U.S.P. 1,410,121 ; *J.*, 1922, 317A.

[74] E.P. 181,879 ; *J.*, 1922, 619A.

[75] *Intern. Sugar J.*, 1922, 533.

After the centrifuging of the massecuite, the molasses (or so-called "green syrup") thrown off is worked up further, since from it a further crop of crystals is obtainable, but before passing it into the vacuum pan for the granulation of these "seconds" it is frequently subjected to a purification treatment. This may consist simply of "saturation" with carbon dioxide or sulphur dioxide, or both, and sometimes filtration follows. It does not appear to have been established that any increase in the purity ratio results from these operations, though it is often suggested that the viscosity of the syrups is diminished (and indeed in the light of the observations made by A. Vasseux[77] regarding the method of dealing with low-purity juice at Oxnard, this may very well be true). A method of endeavouring to raise the purity of the centrifugal syrup (not in general use) is to dilute, heat, lime, and carbonate, that is, once again to repeat the carbonatation process applied to the juices at an earlier stage of the manufacture. However, A. Claassen,[78] an acknowledged authority, states that "since lime here acts upon non-sugars, which are present to a considerable extent, just as it does upon the original thin juice, it is clear that a perceptible improvement can be attained by this method only when the original defecation was not sufficiently complete, or was conducted at too low a temperature. It has never been found that the purity of the syrup is increased by the action of lime, but on the other hand, it is said that after this treatment the syrups are more readily crystallised. . . ."

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[76] *Bull. Assoc. Chim. Sucr.*, **38**, 409 ; *J.*, 1922, 909A.

[77] *Loc. cit.*

[78] "Die Zuckerfabrikation," 4th ed., p. 268.

It is now of very great interest for the beet sugar manufacturer to notice that K. Urban,[79] a reliable investigator, has published details of a large number of experiments, showing that by means of what he terms " instantaneous saturation " a large increase in the purity, as well as a considerable diminution of colour and ash, can be realised. His procedure (for which patents have been applied) is the following : Syrup at a concentration of 50°–60° Brix is heated to 90° C., milk of lime added while stirring, and a current of carbon dioxide passed in at the same time, the rate of flow of the latter being so adjusted that a low alkalinity is maintained throughout the operation, say within 0·01–0·10% CaO. In an experiment carried out on the large scale, using 12·5% of lime on the weight of syrup, an increase in the purity ratio of 3·7°, a decrease in the colour of 64%, a decrease in the ash content of 9·7%, and a decrease of the soluble calcium salts of 41·3%, was accomplished. These results are quite phenomenal, especially in view of the belief hitherto held that such impure liquids can hardly be improved by the action of lime followed by carbon dioxide. In the opinion of the reviewer, the effect is not to be accounted for by the chemical action of the lime, or at any rate only in part ; but that here again the impurities mentioned are eliminated by the adsorbing power of the calcium carbonate at the moment of its formation in the body of the syrup. It may also be remarked that the basic idea of this process has long been known, seeing that forty years ago Horsin-Déon, in his work on beet sugar manufacture,[80] suggested the treatment of syrup by " adding milk of lime in thin streams, and at the same time passing in carbon dioxide " ; while De Haan's method of " simultaneous carbonatation " has been operated in certain cane sugar factories in Java for the clarification of the juice with very satisfactory results. However, the particular conditions under which Urban operates do not appear previously to have been applied in the beet factory for the treatment of syrup or unexhausted molasses ; and it will already have been noticed that a rather large quantity of lime, *viz.*, 12·5% of the syrup, was required to produce the results which he has obtained, though, according to his figures, an appreciable increase of purity is shown by the use of less. It, therefore, seems likely that this " instantaneous saturation " process, owing to its considerable purifying effect, and especially to its power of lowering the viscosity, may after further trial be found to be an important improvement, making the working up of these after-products much less difficult than it has hitherto been, as well as increasing the yield; and perhaps also the quality of the second sugar.

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[79] *Z. Zuckerind. Czechoslov.*, 1922, **46**, 323, 344 ; *J.*, 1922, 428A.

[80] " Traité de la Fabrication du Sucre," 1882, p. 144.

THE REFINING INDUSTRY.

Other than the considerable amount of work that has been done during the past year in endeavouring to establish the value of vegetable decolorising carbon as a substitute for animal charcoal (boneblack or "char"), there is hardly anything of importance to record regarding refining, a fact which is regretted, and which is in striking contrast to the activity of the two producing branches of the industry. It is, in fact, possible to mention only three papers of general interest which have recently been communicated, these being: the description by G. M. Rolfe[81] of the new plant at Crockett, California, now the largest sugar-house in the world; the particulars by an anonymous writer[82] of the electrical installation at Baltimore; and lastly the account by P. Beyersdorfer[83] of some useful investigations on the causes of sugar dust explosions. None of these articles, however, calls for comment here, and a mere reiteration of the details already abstracted is unnecessary.

Decolorising Carbons.—Much useful work has been carried out during the past few years with the two-fold object of: (1) preparing materials of a carbonaceous nature having a considerably intenser adsorbing effect than animal charcoal; and (2) applying these to the routine practice of the refinery. There are now a number of carbons on the market, mostly made from materials of vegetable origin by various methods of "activation," which compared with animal charcoal possess many times the power of adsorbing organic and inorganic impurities, that is "gums," colouring matters and salts, from raw sugar liquors. Moreover, their application (that is initially) is simple, involving as it does merely a mixing and filtering operation, using tanks and filter-presses, in place of the bulky char cisterns and rather troublesome Taylor bag filters (which latter are still in use in many refineries). What stands in the way of their extended adoption is the fact that their market price at the present time is 4–6 times that of char, and that consequently their repeated revivification becomes a matter of necessity.

In the case of animal charcoal, revivification involves washing with water, followed by re-burning in special kilns; and the nature of this material is such that it is capable (provided certain conditions are carefully observed) of being handled in this way a great number of times, its decolorising power meanwhile decreasing only comparatively slowly. In regard to its intended rival, treatment with water, a dilute solution of sodium hydroxide, a dilute solution of hydrochloric acid, and also re-burning, are employed, which operations may be applied successively in the order stated, or one or two (*e.g.*, hydrochloric acid and re-burning) may be adopted. Experience has shown that it is by no means every decolorising carbon that is capable of "holding up" (to use a technical colloquialism) to a sufficiently high level after being submitted repeatedly to the treatment indicated, though certain grades appear to have given good results, entitling those who have worked with them to claim that with these particular preparations (and with the use of certain apparatus) their application and revivification can be effected at a lower figure than obtains in the case of animal charcoal. One of these carbons, namely the excellent grade "Norit," has been put into operation here and there in refineries and factories in the United Kingdom, Belgium, Holland, Spain, South Africa, Hong-Kong, Java, Philippine Islands, and the United States of America, generally as a substitute for bone char, but in some instances as an adjunct to that material. Another, which has recently appeared, known as "Darco," appears to be at least as powerful as "Norit" in its effect, and is reported to be giving very promising results in Louisiana, while a factory for its production, capable at present of producing about 7000 tons per annum, has been erected at Marshall, Texas, one of the raw materials used being lignite.[84] Summarising this brief general statement regarding the present position of the innovation, it may be said that the development of the use of decolorising carbons in the sugar industry has been rapid, and that, on the whole, satisfactory progress has been made. But it may be added that probably more has yet to be done before their revivification reaches the state of convenience and economy with which animal charcoal is operated in the refinery of the present day.

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[81] *Intern. Sugar J.*, 1921, 617.

[82] *Ibid.*, 1922, 663.

[83] *Z. Ver. deut. Zuckerind.*, 1922, 475; *J.*, 1922, 830A.

Of the immense amount of literature which has been published on the very interesting subject of the preparation and use of decolorising carbons, it is impossible to find space for more than a comparatively short summary. Hence only those papers which appear to the reviewer to bear on the more salient points of the problem will be noticed, these treating *seriatim* of: methods of preparation; essential qualities of a carbon for sugar work; and technical application and revivification.

Regarding the preparation of decolorising carbons, at first it was thought necessary for the production of a high-power preparation to treat the carbonaceous material (*e.g.*, sawdust) with an alkaline-earth, or a soluble or insoluble salt, to act as "spacing agent," particularly good results being given by lime, zinc chloride, and magnesium chloride.[85] But it would now seem that products having at least as high an adsorbing power as those made by such methods can be produced by treating the mass in the carbonising furnace at some stage with a gas, such as carbon dioxide or steam. This procedure obviates the use of the spacing agent, and furthermore of the rather large amount of hydrochloric acid that is often required to remove it after the completion of carbonisation. A number of different patents relating to activation by means of gas could be cited; but the most notable appear to be those taken out by J. N. A. Sauer,[86] and a perusal of these specifications is recommended to those interested. Then attention should also be directed to the particularly useful work of C. E. Coates,[87] who obtained a product having a decolorising power about 2½ times that of well-known commercial grades by the following procedure: carbonise at 500°–600° C., heat for one hour at 800°–850° C., boil for 2 hrs. with a 20% solution of sodium hydroxide, wash with water, boil with hydrochloric acid, again wash with water, and finally dry. This work, therefore, opens up the possibility of preparing a powerful decolorising material from the waste bagasse of the mill for the production on the plantation of a white granulated sugar, suitable for direct consumption, without the intervention of the usual refining operation.

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[84] *Intern. Sugar J.*, 1922, 483.

[85] *Ann. Repts.*, 1919, 4, 393.

In regard to the essential qualities of a carbon for sugar refining, it may be remarked that those who have turned their attention to methods of producing these preparations do not appear always to have borne in mind the possibility of properties other than an initially high decolorising power being required. Indeed, recent experience has revealed the fact that (so far as our industry is concerned) certain other qualities are at least as important. Thus, in the first place, a hard physical structure is necessary for the material to withstand wear-and-tear, particularly in re-burning. Then it has been found that if the carbon has been ground very finely for the purpose of providing an initially high decolorising power it becomes "slimed up" in use so rapidly by the accumulation of gums and pectins and other colloidal matter, that a thin impenetrable cake is formed in the presses, so that filtration is difficult, and "sweetening-off" becomes too slow to be practicable. This has led W. H. Dunstone[88] to remark that "a degree of fineness of grain is important in supplying the maximum surface for colour adsorption, but this must be modified by the porosity of the grain, and the organic impurity adsorbing quality of the carbon."

Another important property, which every carbon should possess, is the power of adsorbing soluble salts from the liquor under treatment. Bone char possesses this quality in a fairly marked degree

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[86] E.P. 167,195; *J.*, 1921, 686A.

[87] *Intern. Sugar J.*, 1922, 476.

[88] *Ibid.*, 1922, 475.

(owing mainly to its mineral skeleton, as may be proved by experimenting with material from which the carbon has been burnt away); but, in general, decolorising carbons appear to be less active in this respect. Since the amount of molasses which is produced in refining is controlled largely by the amount of soluble so-called melassigenic salts remaining in the liquors submitted to crystallisation, it would appear to follow that the yield of sucrose in the form of the various crops of sugars taken off must be adversely affected. Thus, C. E. Coates[89] has asserted that 25% more molasses is produced in vegetable carbon refining, compared with bone char practice; while W. D. Horne[90] estimates the increase to be as much as 50%. This insinuation regarding the lower yield of sugar realised in carbon application has, however, been controverted by W. H. Dunstone and B. Sandman,[91] who argue that, whereas in the case of bone char the adsorbed salts are largely removed during the sweetening-off operation, and whereas it is customary to return this sweet-water (after its concentration) into the process again in order to avoid loss of sugar, on the other hand, vegetable carbons tenaciously retain the salts adsorbed by them, so that the water resulting from their washing is comparatively low in saline content, introducing only a very small amount of melassigenic matter, when it is used for the melting of the raw sugar. These two writers go further, and assert that in using decolorising carbon the loss of sugar occurring in the various operations (particularly in filtration) is on the whole less than ordinarily; so that ultimately in a refinery employing "Norit" the yield of granulated sugar is 93·3% of the 96° raw sugar treated, a figure which is quite as high as that realised in any well-conducted char house. It is consequently difficult to form an opinion in the matter, and it seems certain that further experience gathered from lengthy large-scale practice is necessary before a conclusion regarding these conflicting views can be reached. In concluding this discussion of the essential qualities which decolorising carbon should possess for use in the sugar-house, it may be stated that the following points (some of which are co-related) should be considered: colour-adsorbing power; salt-adsorbing power; filtering capacity; size, hardness, and porosity of grain; facility with which sweetening-off may be conducted; power of "holding up" after long-continued revivification; and lastly uniformity of quality.

Coming finally to the technical application and revivification of decolorising carbons in refinery practice, the reader is referred to a useful paper by H. H. Dann,[92] who outlines the principal steps involved, the particular preparation concerned being "Darco."

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[89] *Facts about Sugar*, 1922, **14**, 372.

[90] *Ibid.*

[91] *Ibid.*

[92] *Intern. Sugar J.*, 1922, 630; *J.*, 1923, 154A.

Briefly, these steps consist in washing the raw sugar in centrifugals until the crystals remaining have a purity ratio of about 99°; melting this product to a liquor of 60° Brix; treating it at a temperature of 90° C. with the decolorising carbon, using 1½% calculated on the weight of raw sugar treated; filtering through plate-and-frame presses; washing the carbon with water; and revivifying. Emphasis is rightly laid on the importance of the latter operation, and the exercise of careful chemical control during its performance. In the re-use of this carbon it would appear that the best results are obtained by first boiling the spent carbon with water during half an hour (in order to dissolve as completely as possible the soluble organic matter and traces of sugar remaining) and then re-burning, which method of revivification is stated to be the most satisfactory and economical, though "under certain conditions it may be advisable to interpose treatment with concentrated hydrochloric acid between the water washing and the re-burning kiln," so as to reduce the soluble ash content of the carbon to a minimum. It is very evident from this writer's communication that revivification requires close supervision, and he adds that "the necessity for careful and intelligent operation of the revivification process cannot be over-estimated, for upon the proper revivification of a decolorising carbon depends, not only the decolorising power, but likewise a more important factor, *viz.*, the filtering capacity."

Then W. H. Dunstone[93] has also put on record his experience in the revivification of "Norit," and his paper should likewise be studied by those interested in this question, as should also one by R. G. Tillery,[94] who has worked with the same preparation. It is noticeable that these two writers appear to have abandoned the alkali and acid system of revivification formerly advocated, and now rely upon re-burning, alkali treatment being omitted entirely, and acid being applied only occasionally, in order to reduce the salts taken up during the course of use. "Re-burned carbon, especially with an occasional acid treatment, is so much superior to that regenerated either by the acid or by the acid and caustic methods that it is poor economy in every respect to use the chemical treatment as the only means of revivification."

STARCHES AND GUMS.

In this branch of the carbohydrate industry there is very little to report, and it remains only to make brief mention of a few patents. In the manufacture of starch, it has been found by F. H. Campbell[95] that a high yield of this product, practically free from gluten, and in an unchanged condition, can be obtained by acting on wheaten flour with a single proteolytic enzyme (as pepsin or trypsin), which converts the insoluble nitrogenous constituents of the flour into water-soluble substances capable of being removed by washing, neither the starch, nor the cellulose envelope in which it is enclosed, being affected in any way. His actual conditions of working are to subject the wheaten flour to not more than 0·04% of the proteolytic enzyme by heating the enzyme with water and an acid or alkali to a temperature of 40°–50° C.; to add the flour, the mixture being maintained at the temperature stated until the action of the enzyme is complete; and to separate the starch by centrifuging, the traces of remaining acid being removed by washing with water. Another means of separating the gluten in the manufacture of starch has been protected by R. G. Brindle,[96] who aerates the raw diluted product so as to produce a froth, which is maintained in a substantially stable and quiescent state so as to keep the bubbles of the froth from breaking until the starch liquor has drained therefrom, after which it may be subjected to a further aeration until it has reached a condition at which a froth cannot be obtained. It is then subsided, the intermediate layer separating out being withdrawn, and subjected to further aeration.

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[93] *Intern. Sugar J.*, 1922, 478; *J.*, 1922, 910A.
[94] *Ibid.*, 1922, 479; *J.*, 1922, 910A.
[95] E.P. 182,829; *J.*, 1922, 7?7A.

Regarding the preparation of vegetable glues, V. G. Bloede[97] has elaborated a process which consists in forming a paste or jelly of starch by first mixing the dry raw material to a smooth cream with cold water, heating this to a point to which the starch jellifies, and then intimately combining with a starch-coagulating agent, calcium and barium hydroxides being mentioned as suitable materials, while the amount to be used is stated to be "only enough to produce a maximum degree of homogeneity, adhesion, and cohesion in the composition." Lastly, it may be mentioned that A. W. H. Lenders[98] has devised a procedure for the preparation of a dry soluble starch product. A water solution of modified or thin-boiling starch is made by the usual process of acid hydrolysis, then the solution subjected without added ingredients to a temperature which instantaneously evaporates the water and further modifies the starch, the flaky degredation product thus obtained being useful as a textile size, or as a raw material in the manufacture of vegetable glues.

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[96] E.P 159,838; *J.*, 1922, 777A.

[97] U.S.P. 1,396,315; *J.*, 1922, 25A.

[98] U.S.P. 1,418,311; *J.*, 1922, 604A.

THE FERMENTATION INDUSTRIES.

By H. Lloyd Hind, B.Sc., F.I.C.,

Consulting Chemist, London.

This year has seen a great depression in the brewing industry, in large measure due to the continuance of high taxation and consequent high prices for beer, together with the depression in general trade. The output shows a very marked decrease when compared with that of 1914, and may be only about 50% of that year. This fall in consumption has not been marked by any rise in the sale of spirits—indeed, there has been an even greater fall in that direction owing to taxation and consequent high prices.

Both barley and hops have been very adversely affected by wet weather during the harvest, and there has been considerable delay in getting in the crops. From the preliminary statement issued by the Ministry of Agriculture it appears that the British hop crop, with a total of 301,000 cwt., has been above the average of the last ten years by about 10%, and the total produce about 25% in excess of that of last year, with an increased acreage of 5%.

J. Stewart[1] surveys the malting barleys of 1921, which were very much affected by the severe drought of the summer. The total crop was estimated to be about 5% short of the average, and the yield per acre 1½ bushels below the average for the previous ten years. The quantity of fine mellow grain was comparatively small, the majority being prematurely ripened white steely barley. The latter malted indifferently, and it was difficult to get uniform growth. Premature ripening prevented complete development. The skins at the base of the grain were often not sealed together and the germ from lack of protection lost a good deal of its vitality The resultant malts were unsatisfactory, and included a larg proportion of sinkers. Moisture percentage in the barleys average about 13. In Scotland there was intermittent rain during th harvest mellowing the grain, but detracting from its appearance though some formed very useful malt. H. M. Chubb also reporte on the 1921 crop.[2]

M. H. Daly points out[3] that the barleys were extremely difficu to modify, a somewhat lengthy steep and fair quantity of sprinklin liquor being required. The abnormality of the barley found its reflection in the fermentations and that in opposite directions, depending on the course the maltster had taken to overcome the stubbornness of the barley. Some barleys subjected to a process of forcing attained perfect growth without complete modification, while others were definitely undermodified. The latter, in the mash tun, generally showed a deficiency of converting power, the others with a too high percentage of soluble matters gave a too highly nitrogenous wort. Defective purging of worts and unsatisfactory attenuations have been obtained in some cases, while in others there has been a tendency to race.

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[1] *J. Inst. Brewing*, 1922, **28**, 58.

[2] *Ibid.*, 1922, **28**, 232.

[3] *Brewers' J.*, **58**, 685.

W. Windisch draws attention[4] to similarities between the barleys of 1921, and those of 1904 and 1911. With such dry barleys there is not a proper maturation of the proteins, but they generally improve on storage or sweating. This improvement did not come about this year, and the barleys preserved more or less of the faults of great dryness. There was a large proportion of damaged corns, with consequent tendency to mould, and the latter was increased by the difficulty experienced in destroying the mould spores, rendered resistant by the dry weather, by means of lime water etc. Difficulties in brewing followed; saccharification was slow and difficult, especially with raw grain. The beer was without life, and had not the necessary elements to hold the head. Stability was generally very bad. Breweries usually free from infection admitted how easily their beers were attacked by bacteria.

The English barley crop of 1922 was influenced adversely from its earliest stages. An early persistent drought hindered the growth of the young plant, and later on excessive rain and lack of sun has resulted in a crop that is poor in appearance and deficient in quality, the bulk is coarse, discoloured and unripe. No doubt, after sweating some of the barley will malt well, and some of the difficulties encountered last year will not be met with this season, but it is expected that the quantity of high-class malt will be small. Reports from the Continent show that, despite an increased acreage, the crop is smaller, the unfavourable weather, particularly heat and drought in May, having caused a fall per acre. It has also very generally suffered through the excessive rains during the harvest. Roumania and Yugo-Slavia have been more favoured, and good harvests are reported.

D. Neumann writes[5] that, since the war, the difficulty of getting sufficient supplies of barley in Germany has led to interest in winter barley, and its quality has been recently improved.

[4] *Woch. Brau.*, 1922, **39**, 231.
[5] *Ibid.*, 1922, **39**, 121.

THE INSTITUTE OF BREWING.

The year has been marked by a definite step in the direction of raising the status of the operative brewer, and placing him on a level with members of other organised professions. The Institute of Brewing have issued the syllabus of the examinations which they propose to hold, and on the results of which their diploma will be granted.[6] The examination is divided into two parts. The first, qualifying for the Associate Membership, prescribes studies in chemistry, physics, and botany, equivalent to a two years' college course. There will also be papers on brewing and malting technology, and on the micro-biology of the fermentation industries. Part II., the final examination for the diploma, is intended to test more particularly the candidate's knowledge of malting and brewing, and his acquaintance with such subjects as are needed by persons in responsible control. This examination is only open to Associates who have had at least six years' practical experience in a brewery.

MALTING AND BREWING.

Lecturing before the General Assembly of the Old Students of the Brewing School of Nancy, P. Petit[7] gave an interesting résumé of the progress realised in brewing during the last thirty years, and indicated some of the probable lines of advance. He suggested the possibility of the use of suitably-prepared raw grain direct in the mash without previous cooking, and the replacement of the mash-filter by centrifugal separators. Great economies could be looked for in the use of materials without husks as, when employed with a centrifugal separator, sparging and consequent evaporation would be almost dispensed with. Centrifugal machinery will also probably replace beer-filters.

Centrifugal separating and straining machinery is already attracting very considerable interest in breweries and has been applied to the separation of yeast from beer.[8] Other applications will, no doubt, soon follow, such, perhaps, as the separation of wort from hops, and the drying of spent hops. In the Broadbent centrifuge liquid-skimmed yeast or sediment is fed into the cage running at 950 revolutions per minute. The yeast is thrown against the filter-cloth which lines the basket, forming a solid cake, the beer passing through into the outer case.

H. Heron describes[9] the principle of centrifugal strainers, of the above type, and of centrifugal separators in which no filter-cloth is used. In the latter the yeast is deposited on the sides of the drum and the beer passes out at the top or bottom. He suggests the possibility of sterilising beer without affecting its flavour by means of a suitable centrifugal machine, perhaps of the Sharples type.

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[6] *J. Inst. Brewing,* 1922, **28**, 282, 921.

[7] *Brass. et Malt.*, 1922, 15.

[8] *Brewing Trade Rev.*, 1922, **36**, 154.

[9] *J. Inst. Brewing.*, 1922, **28**, 498.

Reports of practical malting experiments come from the Weihenstephan experimental brewery.[10] Steinecker washing and pumping arrangements have been installed in the Doornkaat steeps. The barley is pumped from the first to the second tank, in each of which it is aerated and washed during 24 hours. It is then pumped to the finishing tank, where it is steeped 12 hours and left dry for seven hours, during which time the carbon dioxide is removed by aeration. O. Meindl has published some of the conclusions he draws as to the effect of aeration in the steep and the best way to carry it out.

It is not only in regard to the steep that the question of aeration has been much discussed, but flooring processes, such as that of Kropff, which seek to prevent unnecessary loss on the floor by restriction of aeration, have aroused considerable interest. G. de Geyter[11] sets out to control the unnecessary combustion of endoperm material, which takes place during malting, by aerating the pieces with air whose carbon dioxide content is controlled. The process provides means for regulating both the temperature and respiration of the grain, decreases the losses and increases the extract. It avoids intra-molecular change in the grain, brought about by immersion for an extended period in carbon dioxide, by which alcohol and carbon dioxide are produced, leading, it may be, to greater losses than are caused by respiration.

Landouzy describes[12] the crushing of malt by a moist process in a French brewery giving a malt milk and a thick mass of husks and steely tips. Various advantages are claimed, among which are the elimination of dust and the possibility of carrying the crushing to the limit with a resulting increase in extracts.

Several other methods have been described for increasing extracts, some of which depend on mechanical devices, while others are variations in mash-tun treatment devised with the object of fostering enzymic action. The latter are dealt with later. Among the former is a patent of C. F. Hyde[13] covering a method for separating by suitable milling and screening the steely parts of the grain and treating them separately in a converter previous to mashing them with the main portion of the malt.

J. Rechenberg recommends[14] improvements in the Lazarus process of mash boiling. After peptonisation and saccharification the mash is raised to boiling, the pressure ultimately reaching 1½ atm. This is followed by a reduction of the temperature to 158° F. (70° C.) and addition of diastatic wort to complete conversion and a final increase of temperature to 194° F. (90° C.). An improvement in yield results without impairment of flavour. The percentage of proteins in the grains is lowered while greater palate fullness and increase in viscosity are obtained. The protein rest should be given to get over drainage difficulties, which arise through the decomposition of insufficiently degraded proteins.

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[10] *Z. ges. Brauw.*, 1922, 101, etc.

[11] Belg. P. 291,039.

[12] *Nord Brass.*, 1922, 13.

[13] E.P. 186,161; *J.*, 1922, 912A.

[14] *Z. ges. Brauw.*, 1921, 184; *J.*, 1922, 27A.

O. Steltzner patents[15] a method for mashing in a closed vessel under 2 atm. pressure. Saccharification is facilitated by the liberation of starch through bursting of the cells.

An improvement has been made on the well-known Steel's masher by the addition of a mash regulator devised by T. Crawford. A regular admixture of grist and liquor is maintained by allowing the inflowing mash to fall through a grid attached to the spout of the machine. Variations in pressure on the grid caused by changes in thickness of the mash are translated into control over the quantity of grist admitted by the slide and of the liquor flowing into the Steel. The apparatus is described by the inventor in a paper on "Regularity in Brewing"[16] in which practical methods for the attainment of regularity through every phase of the brewing process are described.

In place of the ordinary copper a new type of steam-heated evaporator, that of Prache and Bouillon, has been installed in a French brewery.[17] It is an inclined, multitubular boiler through which the wort circulates quickly in the opposite direction to the hot water condensed from the steam. The boiling process is made continuous, as fast as the wort passes from the mash tun, with reduced coal consumption and saving of time. The degree of coagulation and caramelisation can be controlled by regulating the flow of the wort and the pressure of the heating steam. A considerable economy of steam is claimed, the 60 or 70% evaporation ratio of a steam-heated copper being increased to 300%.

Following the discussion raised by E. R. Moritz' paper, "Refrigeration and Flocculation,"[18] on the best means to ensure a satisfactory "break" in wort and his advocacy of vertical and horizontal refrigerators in tandem, comes a contribution by F. Emslander,[19] who considers that the type of cooling plant and manner of cooling are only of minor importance in connexion with the flocculation of wort. The formation of a pellicle on the surface of the wort during a rest after boiling is more necessary. If this skin is broken the fragments sink to the bottom and another forms; the proteins tend to accumulate at the surface. A similar pellicle forms on the coolers until the wort reaches 60° C. and here again occasional disturbance of the surface is advisable, but continuous agitation prevents flocculation.

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[15] G.P. 345,755.

[16] *J. Inst. Brewing*, 1922, **28**, 874.

[17] *Ann. Brass. et Dist.*, 1922, **1**, 3.

[18] *J. Inst. Brewing*, 192?, **27**, 521.

[19] *Woch. Brau.*, 1922, **39**, 67.

The Nathan Institut, Zurich,[20] patents a completely enclosed system of cooling and sludge sedimentation for wort under aseptic conditions. The separation of sludge is brought about in an aluminium vessel provided with trays and an external cooling arrangement. Further cooling and aeration are carried on in another closed, externally-cooled vessel of vertical, cylindrical shape. The wort flows smoothly down the inside surface of this and is met by an ascending current of air.

Despite the almost universal belief in the necessity for hot aeration and the provision of all sorts of means to bring it about, it is conceivable that other factors than the aeration are operative. H. B. Wooldridge[21] points out that in his process of brewing, in which the essential point is the exclusion of air from the wort until it arrives in the fermenting vessel, there is no hot aeration, but considerable agitation. No defects in break or brilliance of beer appear to result. The process has proved its suitability for the small breweries which are being erected in the newly-built villages of Belgium and France.

The advantages of closed fermenting vessels have been discussed by Mme. Vanderhagen,[22] who claims that beer fermented in them clarifies more quickly than in open vessels. In addition it filters more easily, and a higher degree of saturation with carbon dioxide gives improved condition. Stability is increased by higher acidity and alcohol content. The system is particularly adapted to top-fermentation beers of low gravity, which have more body than when fermented in open vessels. The only inconvenience is the lowered crop and early degeneration of yeast, which may, however, be counteracted by aerating yeast and wort before pitching.

In the systems usually employed for aerating worts in fermenting vessels, the wort is either sprayed through the air in a more or less dense mass by means of a pump, or air is passed into the wort in bubbles of considerable size. The Lamsen process for carbonating beers has shown the advantage of passing the gas into the beer in a state of very fine division and a similar method is now suggested[23] for the aeration of fermenting worts. The air is forced under a pressure of 5 lb. per square inch, through channels or chambers of porous stone, into the wort.

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[20] E.P. 155,847; *J.*, 1922, 341A.

[21] *J. Inst. Brewing*, 1922, **28**, 318.

[22] *Nord Brass.*, 1922, 3.

Provisional protection has been granted to A. Bexon and G. H. Church [23] for a very convenient adaptation of compressed air in cylinders to wort agitation and aeration.

The danger of air-borne infection is called attention to by O. Overbeck,[24] who describes how he produced a more stable beer by preventing infection from the air by covering his fermenting vessels with sheets.

To facilitate the constant removal of skimmings from fermenting vessels and the rapid filtration of the beer from them, a new device has been patented by P. W. Norman.[25] It consists of a specially-constructed drum attached to the fermenting vessel and serving as the yeast shoot and from which the yeast is removed by compressed air.

Brewing processes based on acidification and peptonisation of the mash continue to attract research and have aroused a considerable amount of practical attention on the Continent in view of the increased extract obtained thereby. This may amount to 6–8% with certain liquors and materials, a gain of considerable financial moment. There is a general opinion that good results are to be anticipated from a careful working out of the process.

M. H. van Laer reviews [26] the methods introduced by Windisch under the names of protein rest and pre-mashing. These are mainly complementary to and intended to correct defects in the malting process, and ensure more complete extraction of short-grown malts of low diastatic power. Degradation, both of soluble and insoluble constituents of the malt, is brought about, part of the increase of extract being due to the conversion of starch set free by the proteolysis of a protecting protein envelope. The process has its drawbacks, however, among which are the liability to infection from lactic acid bacteria, difficulties in filtration, and reduction of keeping qualities.

P. van Cauwenberge [27] has made experimental brewings, with and without flaked maize. The mashing liquor was neutralised to methyl orange by hydrochloric or sulphuric acid and the malt mash was peptonised at 113° F. (45° C.) for an hour. Flaked maize was then added and enough acid to neutralise half the alkalinity of the wort. After saccharification considerable difficulty was found in filtration on account of a viscous layer of proteins, but higher extracts were obtained. Fermentation was very vigorous, attenuation increased, and extraction of hops more thorough. The beers were more susceptible to acetic bacteria in cask than those brewed under ordinary conditions.

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[23] E.P. 184,860.

[24] *Brewers' J.*, 1922, **58**, 686.

[25] E.P. 178,637.

[26] *Pet. J. Brass.*, 1922, **30**, 687

[27] *Ibid.*, 1922, **30**, 254.

M. H. van Laer remarks[28] that the production of the protein slime is contrary to laboratory experience and indicates that insufficient acid was added to yield the optimum conditions for peptonisation. The high attenuation can be prevented by raising the temperature in the mash tun rapidly after peptonisation.

The chief points for successful working of mashing processes depending on acidification and peptonisation are an accurate determination of the alkalinity of the goods, half of which must be neutralised after the first half hour of the protein stand. Highly calcareous waters are better treated with hydrochloric than sulphuric acid.

The usefulness of the newer methods of expressing reactions of media by means of their hydrogen ion concentrations is finding an ever-widening acceptance in the brewing industry as it is in many other technical and scientific processes. They are particularly valuable as a means of control in processes dependent on the activities of micro-organisms and enzymes, both of which are markedly affected by small changes in reaction.

W. Windisch, W. Dietrich, and P. Kolbach have published a number of papers on hydrogen ion concentration in brewing. One of these[29] describes experiments they have made to check the accuracy of Michaelis' very convenient method for its measurement, using the indicators a- and β-dinitrophenols and m- and p-nitrophenols. They find these indicators accurate to $\pm 0{\cdot}2$, when compared with electrometric methods with light beer, and the accuracy was not appreciably affected by diluting the beer two to eight times. Porter can be diluted 40 times without altering its p_H value by more than 0·2.

The same authors with Pröpsting[30] repeated the experiments of Lüers with a view to determine the optimum hydrogen ion concentration for the precipitation and coagulation of proteins in wort, and the influence of the method of boiling on the amount coagulated. They found the optimum to be $p_H = 5{\cdot}4$. Coagulable nitrogen expressed as a percentage of soluble nitrogen was found to be 8·6% at $p_H = 5{\cdot}81$, 16·8% at $p_H = 5{\cdot}45$, and 12·9% at $p_H = 5{\cdot}12$. Boiling with direct heat gave up to 50% more coagulated protein according as a smaller or larger flame was employed.

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[28] *Ibid.*, 1922, **30**, 256.

[29] *Woch. Brau.*, 1922, **39**, 79.

[30] *Ibid.*, 1922, **39**, 42.

M. H. van Laer also has a series of articles[31] in which he surveys the rôle of acidity in brewing and publishes the results of numerous series of experiments. The various enzymes met with in the mash tun require a faintly acid medium, their optimum being $p_H = 4{\cdot}4$ (neutrality to methyl orange). Experimental brews with distilled water gave $p_H = 6{\cdot}0$ to $6{\cdot}4$, the acidity being slightly higher with well-grown malts and increases by about p_H 0·2 to 0·3 on boiling with hops. Adjuncts reduce the acidity to such an extent if the proportion is high that enzyme activity is greatly restricted. An alkaline liquor of $p_H = 8{\cdot}5$ gave an all-malt wort of $p_H = 6{\cdot}65$, but with 60% of maize grits $p_H = 7{\cdot}1$ was obtained. Saccharification in the mash-tun under these conditions proceeds badly, and the stability of the beer leaves much to be desired. The acidity of the malt depends largely on varying proportions of the primary, secondary, and tertiary phosphates. The acidity of the malt and its lack in the adjuncts have, however, less importance on the reaction of the mash than has the constitution of the brewing liquor.

M. H. van Laer points out[32] that a determination of the reaction of the mashing liquor before and after boiling would be a valuable addition to the usual determinations made in water analysis. Some examples show an increase of acidity on boiling corresponding to a change from p_H 7·7 to p_H 6·7.

The reaction of brewing liquors is also dealt with by A. Fernbach.[33] In malt wort of normal reaction the transformation of maltose is limited to 80% of the original starch, but it can be made complete by the addition of acid up to the point of neutrality to methyl orange. The essential rôle of the salts of lime contained in the water is to change the p_H and the composition of the buffer salts. Calcium carbonate by changing primary to secondary phosphates will reduce the diastatic action as the reaction of the wort approaches that of phenolphthalein, and attenuation and stability will be reduced. Gypsum on the other hand reacts with secondary phosphates and reduces alkalinity.

E. Bekaert draws attention[34] to the very detrimental effect of certain Belgian alkaline mashing liquors, containing 42 to 53 parts per 100,000 of sodium carbonate, on saccharification. The time for complete conversion is extended from 20 minutes to three hours and the loss of extract amounts to 6·5%.

A very suggestive piece of research is that by M. H. Van Laer, on free acidity and stability of beer.[35] Yeasts grow best in slightly acid media, but the optimum p_H depends on the chemical composition and nutritive value of the medium. This was demonstrated by finding the optimum p_H for yeast in Pasteur's mineral nutrient, in unhopped and hopped wort. The figures obtained were $p_H = 6{\cdot}8$, $4{\cdot}6$, and $6{\cdot}0$, respectively. The more nutritive the medium the higher the optimum acidity. A change in reaction of the medium from the optimum point in the direction of alkalinity has much greater effect on yeast growth than an increase of acidity. Translating this into practice, great attention must be paid to the reaction of wort and the prevention of any alkalinity.

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[31] *Pet. J. Brass.*, 1922, **30**, 593.
[32] *Ibid.*, 1922, **30**, 593.
[33] *Ann. Brass. et Dist.*, 1922, **18**, 20.
[34] *Bull. Assoc. Anc. Elèves de Gand*, 1922, **22**, 180.
[35] *Pet. J. Brass.*, 1922, **30**, 887.

Experiments with distillery yeast gave the same optimum as for brewery yeast, but yeasts habituated to acid beers thrive better in more acid worts.

Van Laer followed up this work by studying[36] the optima for certain disease-producing bacteria, *Bacillus viscosus Bruxellensis* and *Saccharobacillus pastorianus*. The former has an optimum of $p_H = 5{\cdot}5$ in sweet wort, and in hopped wort both grow best at $p_H = 6{\cdot}8$. That is the optimum reaction, for their growth is more alkaline than that for yeast in the same media. Hopped wort is shown to be a medium more congenial for yeast than is sweet wort. Yeast and *Saccharobacillus* were grown in worts of varying p_H, and it was found that the disease did not develop to any appreciable extent at higher acidities than p_H $5{\cdot}4$, and consequently it appears that the acidity of beers and worts is a factor of fundamental importance in their stability.

Among practical papers on brewing topics may also be mentioned a paper on the delivery of beer in bulk, by A. H. Paul,[37] a series of articles on "Wort production," in the *Brewing Trade Review*, by F. M. Maynard, and the completion of a series in the *Brewers' Journal* by the same author, on "Lager beer brewing." The use of oil-fuel in breweries has been dealt with by G. Jones,[38] and by P. K. Le May and J. D. Lickley.[39]

A rapid and accurate method for calibration of storage tanks has been described by J. W. M'David.[40]

The position and prospects of the brewing industry in Canada have been discussed by H. Molson.[41]

Books published or reviewed during the year include "Malterie-Brasserie," by E. Boullanger, an excellent practical handbook on brewing, and Vols. III. and IV. of Thorpe's "Dictionary of Applied Chemistry," with articles on fermentation, etc.

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[36] *Ibid.*, 1922, **30**, 910.

[37] *J. Inst. Brewing*, 1922, **28**, 794.

[38] *Ibid.*, 1922, **28**, 213.

[39] *Ibid.*, 1922, **28**, 718.

[40] *J.*, 1922, 295T.

[41] *J. Inst. Brewing*, 1922, **28**, 536.

In a paper[42] on the micro-biology of cider making, B. T. P. Barker gives a review of the work which has been conducted at the National Fruit and Cider Institute, Long Ashton, on the biological side of cider making.

During the year there have been a number of communications on the influences governing some of the more important properties of beer. A. Fernbach has a paper on head formation.[43] He points out that, as beer acts from a physical point of view as a solution of carbon dioxide, the theory of the existence in it of combined carbon dioxide must be rejected. The present conception is that beer owes its viscosity to the presence of colloids and that these hold the gas by adsorption.

One of the most disconcerting forms of haze to which beer is liable is that which occurs in pasteurised beer after lengthy storage, or more rapidly on cooling. A. Visez discusses[44] this question and suggests that it is due to a complex of tannin and albumin. The colloid constituents of beer take up a very delicate state of equilibrium during storage, and this is very easily upset by such agents as heat, or by the extraction of alkalis from the glass.

Glutin turbidity, palate fullness, and head retention are discussed by F. Emslander.[45] Glutin is a protein of emulsoid character, and occurs in bright beer in a state approaching true solution. Chilling causes it to coalesce to form visible globules, which attract suspensoid particles of coagulated protein to their surface. Palate fullness he considers to be due to the emulsoid proteins and hop resins by virtue of their capacity for spreading out in thin oil-like films over the nerves of taste. These same constituents are probably responsible for the head-retaining properties of beer, owing to their capacity for spreading out into extremely fine films, which strengthen the walls of the gas bubbles.

The very difficult domain of colloid chemistry has also been entered by Clerk Ranken, in his study[46] of the "Influences affecting the bitterness of beer." The substances which produce the bitterness form colloid-solutions, and the greater their dispersion the greater will be the bitterness; the latter is not dependent on the amount of the bitter substances in beer. The α- and β-acids of the soft resins produce the bitterness; their dispersion is low, but increased by alkalis (alkaline brewing liquor). Acids have the contrary effect and diminish bitter flavour. A large proportion of the bitter acids is removed by adsorption at the surface of the proteins coagulated in the copper. Hence the importance of a good break, from the flavour point of view, and of the removal of any sludge that passes to the fermenting vessel and gets thrown up with the first heads.

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[42] *J. Inst. Brewing*, 1922, **28**, 517.

[43] *Ann. Brass. et Dist.*, 1922, **21**, No. 2.

[44] *Bull. Assoc. des Anc. Elèves Louvain*, Jan., 1922.

[45] *Woch. Brau.*, 1922, **39**, 115.

[46] *J. Inst. Brewing*, 1922, **28**, 456.

Ropiness is one of the most troublesome maladies to which beer is subject, and there has always been considerable difficulty in its study, on account of the reluctance of the causative bacteria to grow in the usual media. P. Hampshire has accordingly devised[47] a nutritive medium reproducing as nearly as possible the conditions obtaining in bottled beer. Using this medium he has isolated[48] a bacterium, which he calls *Bacterium R.*, related to the Acetobacter group, which produces ropiness in absence of air, but not under aerobic conditions. Grown together with yeast in air it can, however, produce ropiness.

THE INSTITUTE OF BREWING RESEARCH SCHEME.

An account of the work done under the Research Scheme of the Institute of Brewing must necessarily take an important place in a survey of the research work connected with the British fermentation industries. The three sub-committees entrusted with the different lines of investigation all issue reports. Those published are mainly of a preliminary character, although that on timber reports the conclusion of the first stage of the research. In each case, however, some definite results have already emerged and give considerable encouragement to the further prosecution of the investigations. Those on hops are, in part, being carried out on a practical cultural and brewing scale, and, in part, at the laboratories of the College of Technology, Manchester. The Ministry of Agriculture has marked its appreciation of the importance of the practical trial and growth of new and promising varieties at the East Malling Research Station and Wye College, by bearing a share of the expenses. No report has, so far, been published of the results of the brewing experiments, but their tendency has been indicated by the President of the Institute, in a speech at Wye College, in which he sounded a note of warning against the planting of a certain well-known variety, Tolhursts, which, although it has many cultural advantages, appears to compare badly in brewing value with other varieties.

Hop Research.

The second report[49] of the Research Committee covers the period from May 23rd, 1921, to March 14th, 1922. The work on hops has been divided into five parts :—

(1) *The breeding of new varieties*, which will produce a heavy yield of hops, resistant to disease, and at the same time contain

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[47] *Bur. Bio-Tech. Bull. No.* 5, 1922, 128.

[48] *Ibid.*, 1922, *No.* 6, 179.

[49] *J. Inst. Brewing*, 1922, **28**, 287.

the highest possible amount of resins. This is carried on at the nursery and experimental hop gardens of Wye College, where, in the 2¾ acres, there are about 5000 new seedling varieties under trial. Thirty-two promising varieties were transferred during the year to the East Malling Research Station for tests on a larger scale. Seedlings immune to mould have been raised from the Golden Hop.

The East Malling Research Station has been extended so that an additional six acres is allotted to hops, permitting of a considerable widening of the scope of the work there. "Nettlehead" disease attacked both gardens, and its cause is under investigation by V. H. Blackman and Miss Lacey.

(2) *Manurial experiments.* An acre has been set aside by F. Ivo Neame at Chilham, and by T. J. Nicolson, at Horsmonden, each divided into twelve plots. These have been treated with different manures to ascertain their effect on the brewing value of the hops. As this was the first year of manuring, differences in the composition of the hops can hardly yet be manifest.

(3) *Drying experiments.* Five experimental kilns have been erected at Beltring. They are designed to keep the various factors concerned in the process of drying under strict control in order to ascertain the ideal conditions. Twenty-two kiln loads were dried during the season. A. H. Burgess later[50] gives a full report of the work done at these kilns.

(4) *Testing hops for their brewing value.* The first series of actual trials at a brewery have been carried out. In view of their importance results will not be published until confirmed by other series.

(5) *Chemical investigations.* F. L. Pyman is carrying out researches at the College of Technology, Manchester, with the object of isolating and determining the constituents of the hop on which the preservative properties depend.

In a preliminary report[51] on these investigations Pyman states that, so far, his work, and that of his colleagues, H. Rogerson and T. K. Walker, has been directed to the isolation and identification of the preservative principles, and with that end in view they proceeded to submit the resins soluble in light petroleum to fractional separation. The existence of α-hop bitter acid, humulon, and β-hop bitter acid, lupulon, is confirmed. Lactaric acid, found for the first time in hops, was isolated as one of the products of the fractional extraction, but the general method was found to be unsuitable, largely from the difficulty of obtaining crystalline products, and other methods are now under investigation.

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[50] *J. Inst. Brewing*, 1922, **28**, 579.

[51] *Ibid.*, 1922, **28**, 929.

E. S. Salmon[52] reports on the progress of the trials of new varieties of hops and the results of the growth of seven commercial varieties at East Malling. Attention is being directed to the production of new varieties by crossing sorts which are known to have certain distinctive good properties with others in which these are lacking, but which possess other good qualities. For instance, it is desirable to combine in one the preservative power of Oregon hops with the delicacy of aroma of Kent Goldings, and to impart immunity to disease to otherwise good varieties. Analyses and physical valuation are given of the varieties grown, and, in several cases, very useful crosses have been obtained, notably that between the Oregon Cluster and an English male hop. Dry hopping experiments at a brewery add confirmation of the success of the efforts to produce good new varieties.

Investigations into the best means of raising the standard of hop cultivation have also been carried out in France under a Commission appointed by the Government in 1921. F. and Mme. Moreau on the botanical side developed a method for expressing the density of the cone, depending on measurements of the length of strig and the number of nodes. Dividing the sample into classes of different densities, that class which contains the greatest number of cones is called the "mode." Moreau drew the conclusion that there was a close connexion between this and the brewing value of the hop.

E. S. Salmon and H. Wormald criticise[53] the indiscriminate application of this principle to hops of different countries, pointing out that a Tolhurst hop had a higher mode than an Oregon far superior in brewing value, but consider that it may be useful in the evaluation of certain classes of hops and as a means of detecting admixture in any one sample.

Moreau also arrived at the conclusion that pollination was necessary to cause perfect development in the damp climate of England, Denmark, and America. Salmon and Wormald on the other hand point out that such hops as Goldings, with fewer flowers on the cone, would not grow out to good size cones without pollination in any climate, while hops of fair size would develop even without fertilisation from the varieties grown on the Continent which have more flowers and petals on the cone. They also question the point that the value of the hop is reduced by the reduced density consequent on the increased length of the cone produced after fertilisation, without any increase in the number of nodes. Moreau recognises the increases of resin produced per acre as a result of fertilisation and concludes that it is important to know, for any particular variety and climate, how far the depreciation consequent on fertilisation is compensated by produce per acre.

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[52] *J. Inst. Brewing*, 1922, **28**, 854.

[53] *Ibid.*, 1922, **28**, 549.

C. A. W. Duffield has investigated the "eelworm disease" or "nettlehead," which occurs at East Malling, and suggests that it belongs to the class of diseases known as "mosaic," believed to be due to ultra-microscopic organisms present in the sap of the plant.

E. S. Salmon and H. Wormald give an account[54] of this disease, known as hop canker or "growing off." It is brought about by the attacks of a fungus of *Fusarium* type at the base of the bine and causes considerable damage. They also describe the preventive measures available. E. S. Salmon and H. Wormald have also published a "Study of the variation in seedlings of the wild hop,"[55] and E. S. Salmon a paper on "Forms of hop resistant to mildew."[56]

Barley Research.

The advisory sub-committee on barley came to the conclusion that the best line of action for the research on barley would be to endeavour further to elucidate the much discussed nitrogen question. As a preliminary they invited H. F. E. Hulton to review the published literature relating to the evaluation of barley from the nitrogen standpoint. His report is a comprehensive summary[57] of previous work, and a valuable basis for the further operations of this committee.

The objects of the research are: (1) to ascertain and define as precisely as possible the requirements of the maltster and brewer, and (2) to ascertain the means by which farmers can satisfactorily fulfil these requirements with profit to themselves.

It was decided to deal, firstly, with the second problem. Although it seems certain that environmental factors alter the malting quality of barley, there appears to be no very definite knowledge of the effect of fertilisers. It has, therefore, been decided to carry out experiments in the best barley-growing districts of the country, and also at Rothamsted, plots being cultivated at each place under five different manurial conditions. The barleys grown will be malted and analyses made of both barley and resultant malt.

A useful tool has been forged for the analyses of the samples of these growths by A. R. Ling[58] in the elaboration of the method for determination of starch suggested by H. T. Brown and his co-workers. These authors showed that under certain conditions hydrolysis of starch by diastase led to the formation of 84·4 parts of maltose from 100 parts of starch. This relation depends on the use of a malt of a diastatic power of 80° as the source of the diastase for the conversion. Ling and his colleagues have made the method available for use with any malt by determining the proportion of maltose formed when using malts of other diastatic capacity and constructing a curve based on their results. They have also shown the applicability of the method to the estimation of starch in barley and wheat.

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[54] *J. Min. Agric.*, 1922, **29**, 354.

[55] *J. of Genetics*, 1921, **11**, 241.

[56] *Annals of Applied Biology*, 1921, **8**, 146.

[57] *J. Inst. Brewing*, 1922, **28**, 33.

[58] *Ibid.*, 1922, **28**, 838; *J.*, 1923, 48T.

Timber Research.

The research on timber[59] for cask-making has been carried to a point at which it is necessary to transfer the work from laboratories in this country to the forests and laboratories of the country of origin of the timber. In view of the great commercial importance of the questions to be settled, it is anticipated that the United States Department of Forestry will favourably entertain the suggestion of the Institute of Brewing that further investigation be carried on in America.

The research originated from the desire to find out the cause of the objectionable flavours so often imparted to beer by storage in casks of American oak, and the importance of finding an alternative source of supply to Baltic oak, in view of the possible recurrence of conditions which would render North European supplies unobtainable.

Chemical investigations carried out at the Imperial College of Science and Technology under the direction of S. B. Schryver have indicated[60] that the difference in value of the various timbers for cask-making is due, not to any specific extractive which imparts a deleterious flavour to the beer, but rather to fundamental differences in the chemical and physical properties of the timbers themselves. It was found that the satisfactory staves examined were, in general, more permeable than the unsatisfactory, and that, in consequence, any flavouring matter they contained would be more readily washed out in the preliminary cask treatment, and extractives left in the less permeable unsatisfactory timber after seasoning would diffuse out less quickly, and, therefore, taint successive quantities of beer.

The botanical work was carried out under the direction of P. Groom and showed[61] that the bad flavours imparted to beer were not due to any microbial flora in the wood. In regard to the structure of the wood, the staves examined were all made of heart wood and the more pervious sap wood was not found. It was pointed out that "red oak" was structurally unsuitable for casks but that the "white oaks" of the United States, being more impervious, were applicable to that use. The conclusion arrived at was that the unsatisfactory nature of the wood was due to the use of an inappropriate species, a tree felled at the wrong season, or the employment of heart wood that is too young. These possibilities can only be thoroughly investigated at the place of origin of the timber.

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[59] *J. Inst. Brewing*, 1922, **28**, 294.
[60] *Ibid.*, 1922, **28**, 678.
[61] *Ibid.*, 1922, **28**, 645.

Among other practical and scientific contributions that have appeared during the year on similar subjects to those investigated under the Institute of Brewing Research scheme, the following may be referred to.

A practical paper by H. C. Sweatman on the timber for casks.[62] The author considers that in the future more suitable timber will be imported from America.

A method for the avoidance of any trouble through contact of beer with the wood of the cask has been patented by T. A. Woodhead,[63] the specification covering a process for building casks from staves previously covered with aluminium.

H. U. Harrow has some "Notes on cask cleanliness"[64] in which he points out how easily infection of beer may be caused by lack of cleanliness in casks, and describes a simple method for investigating the state of the cask plant.

W. Windisch, W. Dietrich, F. Grohn, and P. Kolbach[65] have elaborated a method for the quantitative determination of humulon. The rate of degradation of humulon in wort boiling, they find, depends on the reaction of the wort. A strong acidity causes the humulon to coagulate. With a $p_H = 5{\cdot}5$, 24% of the bitter acid is transformed within an hour, and 50% in about two hours. These results have a practical bearing on the length of boil and the alkalinity of the brewing liquor.

H. Heron publishes,[66] in a paper on "The deterioration of hops during storage," a tabulation of the analyses of about 100 samples of hops giving the changes in resins on storage. Curves are plotted showing the percentage of soft resins calculated on total resins. They show that deterioration goes on progressively in cold storage and amounts to 40% in five years compared to 60% deterioration occurring during the same period in ordinary storage. The effect of the weather experienced during picking on the keeping qualities of the hops is marked on the curves by the upsetting of their regularity by the results of the 1915 crop, which possessed very superior keeping qualities compared with succeeding years. Figures are also given which show that when hops which have been cold stored, have been removed and kept under ordinary conditions, deterioration proceeds at the same rate as with non-cold-stored hops. This is contrary to the generally accepted idea that hops deteriorate very rapidly when taken out of cold store. Heron considers the explanation of this mistaken idea is that the value of the hops has been judged by their physical characteristics, based on the idea that little or no change has taken place in cold store. It is necessary to appreciate that the rate of change in the oils caused by atmospheric oxidation has been little checked by cold storage, that the resins have altered not a little but that the decay of the hop cones has been entirely checked.

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[62] *Ibid.*, 1922, **28**, 402.

[63] E.P. 176,391.

[64] *J. Inst. Brewing*, 1922, **28**, 898.

[65] *Woch. Brau.*, 1922, **39**, 42.

[66] *J. Inst. Brewing*, 1922, **28**, 171.

There has been a series of practical articles by A. Amos on the cultivation of the hop crop,[67] and another on trials of new varieties of cereals by E. S. Beaven.[68]

STARCH.

For many years J. C. Irvine has been carrying on research at St. Andrews, on the constitution of the carbohydrates. The work has now reached a point where deductions as to the structure of the more complex carbohydrates, such as starch, inulin, and cellulose, are being drawn.[69] The basis of the work has been the production and characterisation of methoxy derivatives of many of the best-known sugars to serve afterwards as evidence of the structure of the more complex carbohydrates from which they may ultimately be obtained.

G. Malfitano and M. Cattoire have identified[70] amylocellulose as a compound of silica and $C_6H_{10}O_5$ molecules, whilst amylopectin is a phosphoric acid carbohydrate complex. They have detected varying quantities of silica in the amylocellulose of different starches, from 6 mg. per 100 g. in potato starch to 29 mg. in maize starch.

ENZYMES.

M. H. Van Laer has published under the title of "La diastase du malt,"[71] the collected but not quite completed work of his father, the late Henri Van Laer. It is an excellent presentation of the subject of enzymes and study of the phenomena which they bring about in the course of malting and brewing.

E. F. Armstrong has a paper[72] on "Enzyme action in the light of modern theories of catalysis," his object being to show that the behaviour of enzymes is in harmony with that of other catalysts, and that their highly-specialised behaviour affords additional evidence of the intermediate compound theory of catalysis.

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[67] *J. Min. Agric.*, 1922, **28**, 891, etc.; **29**, 30, etc.

[68] *Ibid.*, 1922, **29**, 337, etc.

[69] *Chem. Soc. Trans.*, 1922, **121**, 716; Brit. Assoc., 1922, Pres. Add. Chem. Sect.

[70] *Ann. Brass. et Dist.*, 1922, **20**, 291.

[71] Pub. Hoste, Gand, 1922.

[72] *J.*, 1922, 110T.

"The chemistry of enzyme action" is the title of an addition to the American Chemical Society monographs, by K. G. Falk, dealing fully with the enzymes from their chemical aspect.

M. H. Van Laer,[73] developing his view that the activity of hydrolytic enzymes is due to the adsorption at the surface of their particles of both substrate and hydrogen ions, explains the existence of an optimum hydrogen ion concentration by the counterbalancing, at that point, of the increase of activity due to temperature by the injurious coagulating action of the hydrogen ions. He makes the suggestive point that an enzyme capable of acting on different substances should have the same optimum for all. The same optimum hydrogen ion concentration is found for diastatic and proteolytic activities, and this optimum also holds for the hydrolysis of esters and amygdalin by the enzymes of malt.

Cattali and Stern consider[74] that there is no difference between oxidising and reducing enzymes, and that the mechanism of all enzymes which split off water is identical, the different results depending on the way the ions act on the substrate. They classify enzymes into hydrotases, hydrolases, and oxy-reductases. In the last the OH ions combine with one molecule, the H ions with another; catalase is an example.

Amylase.

J. L. Baker and H. F. E. Hulton, in continuance of earlier work of their own,[75] and of Ford and Guthrie,[76] studied the effect of papain on barley[77] from which albumins and soluble amylase, edestin and hordein, had been extracted by water, salt solution, and alcohol, respectively. They find that the amylase liberated by papain is produced mainly from the hordeins, and as papain does not liberate amylase from isolated hordein, or from barley which has been boiled, it follows that it breaks down a pre-existent insoluble enzyme complex to form the soluble amylase.

U. Effront shows[78] that considerable changes are brought about in enzymes on filtration through paper by selective adsorption on the paper of the colloid active substance. He indicates the possibility of using the adsorbent power of cellulose in the preparation of certain enzymes.

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[73] *Bull. Soc. Chim. Belg.*, 1921, **30**, 261; *J.*, 1922, **28A.**

[74] *Arch. Intern. Philos.*, **18**, 403.

[75] *J.*, 1908, 27.

[76] *J. Inst. Brewing*, 1908, **14.**

[77] *Chem. Soc. Trans.*, 1922, **121**, 1929; *J.*, **1922, 871A.**

[78] *Comptes rend. Soc. Biol.*, **86**, 271.

H. Lüers and W. Wasmund have contributions[79] on the mode of action of amylase, which is complicated by the colloidal nature of the substrate starch. They investigated the influence of various factors, and consider that the degradation of starch does not correspond to a mono-molecular process. The Kjeldahl law of proportionality holds for the concentration of the enzyme.

Proteolytic Enzymes.

H. Lundin, in a paper[80] on the proteolytic enzymes of malt, sets out a comparison of the proteolytic enzymes of different origin, as follows :—

Animal origin.	*Yeast.*	*Malt.*
Pepsin.	Pepsin.	Peptase.
Opt. reaction .. p_H 1·5	p_H 4 to 4·5	Malt .. .. p_H=3·7 to 4·3 Green malt .. p_H=3·2 Rootlets .. No peptase
Trypsin of pancreas.	*Trypsin.*	*Tryptase.*
Opt. reaction .. p_H=8·0	p_H = 7·0	Green malt .. p_H=6·3 Rootlets .. p_H=6·3

The autolysis of malt and of the rootlets is the result of the combined action of the proteolytic enzymes found there. The protein degradation brought about by these enzymes can only occur when the reaction of the medium permits their simultaneous action. Optimum reaction for autolysis is: for kilned malt, p_H=4·3 to 5·0; for green malt, 4·4, and for rootlets, 6·3.

P. Nottin[81] has examined from a yeast-making point of view the saccharification and proteolysis of raw and cooked maize, and finds that there is a peptase in raw maize which solubilises the proteins of maize in a way that the peptase of malt cannot do. To get the maximum amount of soluble nitrogen in the wort from maize, it is therefore necessary to digest it for some time at a temperature below that at which this peptase will be destroyed, and afterwards boil it, rather than boil it straight away, before proceeding to saccharification. On this he has devised a process to get the maximum yeast output from a maize mash. In a distillery raw grain wort, the maize maltase transforms the maltose to dextrose, and there is no resting stage in the saccharification, such as when amylase converts starch to maltose.

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[79] *Fermentforschung*, 1922, 169, 235.
[80] *Biochem. Zeits.*, 1922, **131**, 193.
[81] *Bull. Assoc. Chim. Sucr.*, 1922, **39**, 362.

YEAST AND FERMENTATION.

The centenary of Pasteur's birth fell on December 27th, 1922, and celebrations in honour of his work and memory will take place at the opening of the Exhibition at Strasbourg, in May, 1923. The appearance of an excellent biography, "Pasteur and his Work," by L. Descour, translated from the French by A. F. and B. H. Wedd, is very timely. Much interest has in consequence been centred in the historical aspect of the theories of fermentation associated with his name, and several investigations tend to support his view that fermentation is in some respects an alternative to respiration.

F. Hayduck and H. Haehn contribute[82] a series of articles on the problem of zymase formation in yeast. They adopt the hypothesis that it is formed from protoplasm and is linked therewith, but can exist under certain conditions in the free state. Bottom yeast grown under restricted air supplies secretes zymase to such an extent in presence of ample supplies of nutriment that free zymase is liberated. Spirit yeast is grown under aerobic conditions for rapid reproduction and the amount of zymase is restricted. They experimented with a torula that was grown in Germany during the war for foodstuffs on account of its easy digestibility and enormous reproductive power. In contradistinction to beer yeast it was low in zymase and high in catalase, but if respiration is repressed the zymase content is increased and catalase diminished and its fermentative activity improved until it surpasses that of the spirit yeast.

The influence of air on yeast-growth is again referred to by A. Slator,[83] who reports that exclusion of air was not perfect in the experiments recorded last year,[84] and when these were repeated under stricter conditions, small seedings of yeast grew with difficulty and many of the cells died; the entrance of traces of air caused increased growth.

The rate of reproduction of yeast has been studied by N. Clark.[85]

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[82] *Woch. Brau.*, 1922, **39**, 97, etc.

[83] *J.*, 1922, 111R.

[84] *Chem. Soc. Trans.*, 1921, **119**, 115.

[85] *J. Phys. Chem.*, 1922, **26**, 42; *J.*, 1922, 340A.

The deterioration of yeast on storage with pure culture apparatus has frequently been noted. K. Geys shows[86] that the flocculating power gradually diminishes, and later lots taken from the culture apparatus gave powdery yeasts in the fermenting vessels. To avoid this deterioration, wort of such strength should be used that it shall not be exhausted long before the yeast is required.

Bernfeld finds[87] that the quality or degeneration of yeast can be measured by the intensity of the stain produced by alkana or Soudan III on the fatty constituents. The age and generation of pitching yeast can be determined in this way.

The profound modification brought about in the products of fermentation by the presence of different chemical substances is well known. Neuberg calls the formation of aldehyde and glycerin in the presence of sulphites the second form of fermentation, and that of alcohol, acetic acid, and glycerol in presence of alkalis the third form. H. Kumagawa has examined[88] the result of carrying out fermentations with Japanese yeasts in presence of these reagents, and finds that *S. saké* can support even higher concentrations of sulphite than the German yeast, and, consequently, give larger quantities of aldehyde and glycerol, 19·5% and 39·18%, respectively, having been obtained from hexose.

The researches of de Fazi[89] on the acceleration of fermentation by ultra-violet rays have been confirmed by P. Lindner,[90] who records an enormous increase in the fermentative activity of bottom yeast—23 times as much carbon dioxide having been produced in 24 hours as in the comparative fermentation without the rays. In thin layers without agitation the yeast-cells are killed by the light from a mercury vapour lamp, but in bulk these conditions do not apply, and this no doubt explains de Fazi's statement that the rays were not detrimental to the yeast.

The lethal effect of ultra-violet radiation on micro-organisms has been put to a very ingenious use by J. W. C. Topley, J. E. Barnard and G. S. Wilson[91] in the preparation of pure cultures. One selected cell in a mount is protected by a droplet of mercury from the ultra-violet rays, which kill every other cell.

The stimulating effect of various substances on the fermentative activity of yeast has received attention from several investigators. S. Fraenkel and A. Scharf find[92] that in general extracts of vegetables rich in vitamins have a relatively high stimulating effect on fermentation.

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[86] *Z. ges. Brauw.*, 1922, **45**, 51.
[87] *Woch. Brau.*, 1922, **39**, 195.
[88] *Biochem. Zeits.*, 1922, **131**, 148.
[89] *J. Inst. Brewing*, 1916, **22**, 24.
[90] *Woch. Brau.*, 1922, **39**, 166.
[91] *J. Hygiene*, 1921, **20**, 221.
[92] *Biochem. Zeits.*, 1922, **127**, 227.

S. Fraenkel and J. Hager have studied[93] the action of a large number of extracts from the organs of animals and find that, with the exception of marrow, they stimulate fermentation.

E. Abderhalden found[94] that addition of animal charcoal produced a lasting acceleration in the fermentation of glucose solution, probably associated with the formation or fixation of acetaldehyde. Neuberg found that acetaldehyde at very low concentrations accelerates fermentation, but Abderhalden's experiments show[95] that at a concentration of 0·35 g. per 20 c.c. it entirely prevents the fermentation of dextrose by yeast.

Inouye,[96] working with Japanese bottom yeast, confirms the acceleration of fermentation by such compounds as ketonic acids and ketones, aldehyde having a permanent beneficial effect.

It is generally recognised that toxic substances act as stimulants when employed in very weak doses; among other substances, salicylic acid, arsenious acid, and iodine have been quoted in this connexion. G. Joachimoglu, however, gives some results[97] which contradict the general application of this belief, and point to the possibility that yeasts act differently to animal cells in relation to toxic substances.

H. von Euler and K. Myrbäck find[98] that toluene, chloroform, and ether have practically no action on the fermentative activity of expressed yeast juice, although they reduce the originally much greater activity of living yeast to a very low value. In the drying of yeast a considerable amount of the zymase appears to be liberated from association with the protoplasm, and the fermentative activity of the dried yeast is reduced by toluene, although to a much less extent than living yeast.

The question of nitrogenous nutrition is one of the most important factors governing yeast growth, and, hitherto, asparagine has been very largely used as a source of nitrogen in yeast nutrient solutions. A. Tait and L. Fletcher show[99] that its selection is unfortunate, as very great differences are obtained when working with a nutrient medium containing asparagine when compared with one in which an extract of malt rootlets is used as the source of nitrogen. They ascribe the toxic effect on the yeast to the formation of malic acid and a higher acidity than is suitable for the yeast growth and to excess of ammonium salts. The application to practical brewing occurs when a wort contains an excessive amount of amino acids, as it does when slack or forced malts have been used. The existence of substances which will, under the necessary conditions, neutralise the acid formed is referred to as of first importance in fermentation.

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[93] *Ibid.*, 1922, **127**, 189.
[94] *Fermentforschung*, 1921, **5**, 89.
[95] *Ibid.*, 1921, **5**, 110.
[96] *Woch. Brau.*, 1922, **39**, 191.
[97] *Biochem. Zeits.*, 1922, **130**, 239.
[98] *Ibid.*, 1922, **126**, 179.
[99] *J. Inst., Brewing*, 1922, **28**, 697.

CARBOLIGASE.

J. Hirsch has carried out[100] some experiments which seem to throw light on the transformation of pyruvic acid by fermentation. The production of acetaldehyde hardly ever exceeds 50% and it appears that the remainder of the acetaldehyde may be transformed to acetylmethylcarbinol, the latter being formed by condensation of two molecules of acetaldehyde by the action of the enzyme carboligase.

VITAMINS.

Interest in vitamins is continued, and the appearance of a book, "The Vitamins," by H. C. Sherman and S. L. Smith[101] is very welcome.

A. Seidell[102] gives a method for the preparation of vitamin B from fresh yeast, in the form of an activated fuller's earth. The vitamin B content of the preparation is about twice as great as in that prepared from autolysed yeast. He further obtains[103] highly active vitamin preparations from the activated fuller's earth, stable in solution or in the dry state.

C. Funk and H. E. Dubin isolated[104] a substance from autolysed yeast different from vitamin B, having no effect on the growth of rats or polyneuritic pigeons, though accelerating the growth of yeast. They consider it probable that all previous experiments on vitamin B have been made on mixtures of the latter with this substance, which they name provisionally vitamin D.

C. Eijkman, C. J. C. Van Hoogenhuijze, and T. J. G. Derks[105] find that only yeasts that have been developed in media containing the antineuritic vitamin contain the vitamin, but media in which the vitamins have been destroyed by heat will furnish a yeast containing them. Yeast therefore appears to be unable to synthesise vitamins except from the products of their decomposition.

ANALYSIS.

A revised schedule[106] of "Standard Methods of Analysis" applicable to pale malts and to coloured malts and caramels has been issued by the Institute of Brewing. Some slight alterations in the direction of simplification, and tending to greater accuracy, have been made.

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[100] *Biochem. Zeits.*, 1922, **131**, 178.

[101] New York, 1922.

[102] *U.S. Health Repts.*, April, 1922.

[103] *J. Amer. Chem. Soc.*, 1922, **44**, 2042.

[104] *J. Biol. Chem.*, 1921, **48**, 437 ; *J.*, 1922, 72A.

[105] *Ibid.*, 1922, **50**, 311 ; *J.*, 1922, 305A.

[106] *J. Inst. Brewing*, 1922, **28**, 775.

The drying of barley and malt is a very tedious process in a steam oven, and new methods or apparatus tending to greater rapidity or more complete drying are welcome. K. Mohs has described[107] an apparatus devised by G. H. Meihuizen, of different type to the usual oven, by means of which he claims to get in 50 mins. results comparable with those given by a drying oven in four hours. This advantage is gained by the use of dry air only, compared with the air of fluctuating moisture content as usually employed.

Ling's method for the determination of starch has been alluded to elsewhere.

M. and I. Sborowsky have found[108] in mercurous iodide a new accelerator for the destruction of organic matter in the estimation of nitrogen by the Kjeldahl method. They find it to be 5 to 8 times more energetic than mercury alone.

B. Lampe suggests[109] a standardised method for determining the melting point of pitch, to supersede others in which the personal factor may be more marked, in view of the rather indefinite melting point.

J. Effront proposes[110] to determine the liquefactive power of amylase by a method based on the coagulation of starch paste by iodine. The liquefactive power is expressed by the weight of starch liquefied by 1 gram of the enzyme solution in 1 hr.

A. R. Ling and D. R. Nanji propose[111] to modify the method by which pentoses and pentosans are determined by conversion to furfural by precipitating the latter with phenylhydrazine, and estimating the excess of the precipitant by means of standard iodine and thiosulphate.

Daylight lamps have proved almost a necessity for analytical work when artificial light is needed. The Sheringham lamp,[112] which simulates daylight by eliminating a proportion of the red and yellow light from a half-watt lamp by means of a specially constructed reflector, has proved very suitable for determining colours by the tintometer, and for judging barley, etc. Tests made by W. Singleton[113] with various indicators show that the half-watt lamps fitted with blue glass "daylight" bulbs by the Osram-G.E.C., also give results comparable with daylight.

[107] *Woch. Brau.*, 1922, **39**, 138 ; *cf. J.*, 1921, 569A.

[108] *Ann. Brass. et Dist.*, 1922, **21**, 51.

[109] *Woch. Brau.*, 1922, **39**, 109.

[110] *Comptes rend. Soc. Biol.*, 1922, **86**, 271.

[111] *Biochem. J.*, 1922, **13**, 466.

[112] *Analyst*, 1922, **47**, 419.

[113] *Ibid.*, 424.

CELLULOSE FERMENTATION.

The writer is indebted to Mr. H. Langwell for the following notes on the present state of cellulose fermentation.

The wood distillation industry is, at present, moribund, and is only kept alive by the demands for methyl alcohol, and, to some extent, acetic acid, but the first is the more important. The fermentation of cellulose produces acetic acid and methane very cheaply, and recent developments indicate that formaldehyde and methyl alcohol should be obtainable from the methane in good yield at a low price, so that there should be a good opportunity for the introduction of cellulose fermentation processes in the near future.

Many fibrous materials, *e.g.*, sugar cane megass, papyrus, maize stems, elephant grass, etc., occurring in enormous amounts, are not of practical value for paper-making, on account of the high proportion of pithy matter present. Recent developments in the McRae process for removing this pith mechanically have given promising results, so that there is obtained a pith consisting of nearly pure cellulose of no use for paper-making, and a high-grade product which is excellent for that purpose. The pith portion is a very suitable raw material for the fermentation process, being cheap and already collected to a centre.

Saccharification processes.—H. Terrisse and M. Levy have[114] still further developed the saccharification process for cellulose and wood waste, using 40% hydrochloric acid. This is understood to have been fairly successful on a small scale, the difficulty being the recovery of the acid. Zellstoff-fabrik Waldhof[115] uses sulphuric acid (about 70%), and after saccharification the acid is employed for making superphosphates. Both processes seem likely to develop as they are particularly suitable for highly lignified materials, such as wood. After saccharification the process is an ordinary fermentation process.

In addition to the process just described bacteriological processes may be classified under biological saccharification and direct fermentation. The first has been referred to in " Fuel for Motor Transport " (2nd memo.), p. 13, issued by the Fuel Research Board.[116]

Direct fermentation.—So far the only account published of work along these lines refers to the Power Spirits process now working on a semi-industrial scale. The most resistant celluloses have been proved to ferment almost as rapidly as the sugars and starches. Yields of acetic acid up to 70% of the cellulose fermented have been obtained in 2000 gallon cultures, while alcohol may be obtained up to 70 gallons per ton of cellulose fermented. There are two types of fermentation depending upon the conditions, and not upon the organism (which seems to be the same for both fermentations), so that with pure cellulose either type may be obtained at will. Pure cultures are not necessary, owing to the highly selective nature of the medium. The first type yields carbon dioxide, methane, and acetic acid only; the second a smaller amount of acetic acid, alcohol, hydrogen, and carbon dioxide, but no methane. All carbohydrates from pentose sugars to cellulose yield much the same products under similar conditions. Certain forms of waste cellulose are so cheap and abundant that it is likely that the main products, alcohol, acetic acid (acetone) and methane (formaldehyde and methyl alcohol) will find a market as a motor spirit containing alcohol and acetone, with formaldehyde and methyl alcohol as by-products.

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[114] E.P. 143,212; *J.*, 1921, 405A.

[115] E.P., 147,415; *J.*, 1921, 866A.

[116] Dept. of Sci. and Ind. Research.

G. W. Monier-Williams has published a very clear and useful book, "Power Alcohol: Its Production and Utilisation," in which he traces the development of the motor fuel position, sources of raw materials, and the production of alcohol from cellulose. A fourth volume of Cross and Bevan's book on Cellulose, covering the work of the last ten years, has also been published during the year.

FOODS.

By G. W. MONIER-WILLIAMS, O.B.E., M.C., M.A., Ph.D., F.I.C.,

Ministry of Health, London.

IN reviewing the progress in food chemistry during the past year it will be convenient to deal with the subject on the lines adopted in last year's report. Considerable progress has been made in research work in many of the directions indicated last year, although it cannot be said that many results of striking interest or importance have been achieved during the period under review. Much of the experimental work now being carried out on foodstuffs in this country is conducted under the ægis of the Food Investigation Board of the Department of Scientific and Industrial Research. Their policy of giving first place to research on fundamentals, rather than to *ad hoc* investigations of limited scope, is undoubtedly a wise one. The latter course might be expected to furnish results of more immediate value to the food manufacturer, but it is clear that organised research into the fundamental problems of biochemistry is essential if real progress is to be made.

PROTEINS AND NUTRITION.

An important contribution to the question of the biological value of protein is to be found in a paper by C. J. Martin and R. Robison.[1] After an extremely clear and comprehensive historical survey of the subject, the authors give details of a lengthy series of experiments carried out upon themselves. The biological value of a protein as defined by Karl Thomas in 1909 is the number of parts of body nitrogen replaceable by 100 parts of the nitrogen of the protein. For the protein of whole wheat Thomas found this value to be about 39%, and this is approximately confirmed by Martin and Robison. For milk protein, however, the latter investigators find a biological value of only 51%, as against Thomas' value of 100%, a result which seems to indicate that milk is not so complete a foodstuff as has formerly been supposed. The arduous nature of investigations of this character can be judged from the following extracts from the paper. "In the experiments upon milk we abandoned all attempts to make the basal ration resemble a repast, and drank a suspension of uncooked corn starch in a saturated solution of lactose. This was followed by an alkaline salt mixture and 2 grm. of agar-agar." Again, in referring to another diet: "after the first few days of this diet no desire was felt for this or for any other food, nor did the sight of our first normal meal at the close of the experiment arouse any appetite."

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[1] *Biochem. J.*, 1922, **16**, 407.

G. A. Hartwell[2] points out, as a result of a long series of experiments on lactating rats, the importance of a balanced diet in preventing the onset of pathological symptoms in the young. She found that when diets containing excess protein of various kinds were fed to the mother, even though the diets contained all the supposed essential constituents, the young were adversely affected. The relative amount and nature of the different additions necessary for normal lactation, and for development of the young, varied with each protein. In some cases, *e.g.*, caseinogen, the addition of yeast juice was sufficient, while in others, *e.g.*, egg albumin, yeast extract, although effecting some improvement, was not completely successful.

L. Berczeller[3] has carried out a long series of experiments on the feeding of rats. It was found that the animals when given the choice of different foods were not necessarily attracted by instinct to the most suitable diet, and frequently chose unsuitable combinations leading to early death.

The work carried out recently by W. M. Clifford[4] on the estimation of carnosine in muscular tissue, has been applied to the problem of distinguishing analytically between fresh and cold-stored meat. Carnosine, or β-alanylhistidine, when treated with diazotised sulphanilic acid in sodium carbonate solution, gives a red colour, and by matching the depth of colour with that of a standard solution of methyl orange and Congo red an approximate estimation may be made of the amount of carnosine present. The estimation is made on a watery extract of the meat, from which soluble proteins have been removed by metaphosphoric acid. Twelve samples of English beef examined by this method over a period of two years, showed from 0·96 to 1·1% of carnosine, while five samples of imported beef gave from 0·35 to 0·37%. The accuracy of this method is questioned by G. Hunter,[5] who prefers to precipitate proteins by coagulation at 70° C. in acetic acid solution, and who maintains that various other substances in the extract contribute to the colour produced with the reagent. In most cases, however, the error due to the latter cause is not more than 5%. A more important objection raised by Hunter is that the carnosine content of muscle varies with different members of the same species of animal. Thus, in four rabbits the amounts found varied from

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[2] *Ibid.*, 1922, **16**, 78.

[3] *Biochem. Zeits.*, 1922, **129**, 217, 239, 251, 270, 289, 313, 320; *J.*, [illegible] 479A.

[4] *Biochem. J.*, 1922, **16**, 341; *J.*, 1922, 606A.

[5] *Ibid.*, 1922, **16**, 687.

0·026 to 0·101%, and in four samples of beef from 0·340 to 0·640%. It is not stated, however, whether any of the latter samples had been subjected to cold storage. I. A. Smorodinow[6] finds 0·289% of carnosine in pork, and states that pork is particularly rich in creatine and carnosine, as compared with the flesh of other animals. A reliable method for differentiating between fresh and cold stored meat would be valuable, but the carnosine method would seem not yet to be established on a basis sufficiently sound for this purpose. That the amino acids produced by hydrolysis of the protein of different kinds of flesh may vary considerably in different parts of the same animal is shown by J. L. Rosedale.[7] The greatest differences were found in the lysine content. Thus, the protein from the breast of a chicken gave only 1% of lysine, and from the leg 10%, while the back of a rabbit contained 13% of lysine, as against 5% in the leg muscle. Red meats were found to contain more lysine than white meats.

L. Lüscher[8] has investigated the accuracy of Von Fürth's colorimetric method for the estimation of tryptophane in the products of protein hydrolysis. He maintains that the usual method, which depends on the blue coloration given by tryptophane with formaldehyde and sodium nitrite gives results about 30–50% too high. He proposes to use benzaldehyde in place of formaldehyde and states that the matching of colours is thereby facilitated and more uniform and accurate results obtained.

VITAMINS.

The most important advance of the year in the domain of accessory factors has been the definite recognition of light, particularly sunlight, as a preventive and curative agent in cases of experimental rickets in animals.[9] Although this aspect of the rickets question does not fall strictly within the scope of a review on foods, the subject is so closely bound up with dietary considerations that it may usefully be considered here. In last year's report the view that rickets is a deficiency disease, arising from lack of vitamin A, associated with insufficiency of calcium and phosphorus in the diet, was considered in some detail. Noel Paton and Findlay and their co-workers of the Glasgow School have, on the other hand, maintained that the chief determining factor in rickets is confinement, together with lack of fresh air and exercise. They incline to the view that rickets is of the nature of an infection, and that diet plays only a secondary part. American workers have now shown that rickets can be prevented in rats by exposure of the animals to sunlight. Rats fed on a diet which, under ordinary conditions of confinement, invariably gave rise to rickets, remained entirely free from this disease if exposed to sunlight for a total of 242 hours over a period of 62 days. They conclude that the sunlight in some way raises the efficiency of the body cells, enabling the organism to put into operation regulatory mechanisms which would otherwise have been inoperative or ineffectual. The function of light and of a factor or factors contained in cod-liver oil and certain other foods, is to exert a regulatory influence over the mineral metabolism of the body having to do with bone formation. When the body is deprived of the regulatory action of certain light rays and of the food factors in question, disturbances in the inorganic metabolism of the body are permitted to develop. The value of sunlight and of ultra-violet light in preventing and curing rickets in children has been recognised for many years, and these experiments on rats afford striking confirmation of the known facts as to the geographical and seasonal variation of the disease. Rickets does not occur in the tropics, and in temperate zones it shows almost invariably a steady increase during the winter months. The recognition of the *rôle* played by light, while going far to reconcile the conflicting views hitherto held, would seem still further to complicate the problem. One's mind naturally turns to the body-pigments, such as hæmoglobin, which have the power of absorbing certain light rays, and to the possibility of some substance analogous to vitamin A being produced by photosynthesis in the human skin. If this be the case, it would seem, however, that the mechanism of the photosynthetic process must be different in the two cases. Experience seems to show that sunlight, to be effective in curing rickets in children, must be direct, and that if it reaches the skin through glass, or other absorbent for ultra-violet rays, it loses much of its potency. Plants, on the other hand, can utilise light of long wave length, and can synthesise vitamin A when grown under glass, or when submerged in water.

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[6] *Z. physiol. Chem.*, 1922, **123**, 116; *J.*, 1922, 953A.

[7] *Biochem. J.*, 1922, **16**, 27.

[8] *Ibid.*, 1922, **16**, 556.

[9] G. F. Powers, E. A. Park, P. G. Shipley, E. V. McCollum, and N. Simmonds, *J. Amer. Med. Assoc.*, 1922, **78**, 159.

McCollum and his co-workers[10] have brought forward evidence which indicates that the anti-rachitic factor in cod-liver oil is not the same as that which favours growth, and which, when absent from the diet, produces in rats the affection of the eyes known as xerophthalmia. They have found that if cod-liver oil be heated for 12 to 20 hrs. in the presence of oxygen it loses its vitamin A, as judged by its curative effect on xerophthalmia in rats, but that its property of preventing rickets is not diminished. Vegetable oils are deficient in both factors, with the exception of coc[illegible] oil which contains the anti-rachitic factor but not vitamin A. The function of the anti-rachitic factor appears to be that of stimulating calcium deposition.

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[10] E. V. McCollum, N. Simmonds, and J. E. Becker, *J. Biol. Chem.*[illegible] 53, 293; *J.*, 1922, 873A.

The elucidation of the origin of the vitamin A found in marine animal oils has been carried a step farther by H. L. Jamieson, J. C. Drummond, and K. H. Coward,[11] who have succeeded in growing a marine diatom in pure culture, and in feeding it to rats as the sole source of vitamin A. They find that this diatom is extraordinarily potent in promoting growth, a daily quantity representing only 4 mg. of oil being sufficient for a rat. Thus the oil of this diatom is of much the same order of potency as cod-liver oil, the minimum dose of which for rats was found by S. S. Zilva and M. Miura [12] to be from 1·7 to 5 mg. The close parallelism between the conditions on land and in the sea as regards the occurrence and distribution of vitamin A is emphasised by J. C. Drummond, S. S. Zilva, and K. H. Coward,[13] in a paper summarising some of the results of a visit to the Norwegian cod fisheries in the summer of 1921. In the more northern latitudes it is probable, as pointed out by Moore, that owing to the limiting angle of refraction of light, the amount of sunlight penetrating below the surface of the sea in winter is very small. As the altitude of the sun increases in spring there occurs a rapid multiplication of diatoms and other minute plant life. These diatoms contain the characteristic pigment, fuco-xanthin, together with chlorophyll, carrotene, and xanthophyll, and are able to synthesise vitamin A precisely in the same way as green land plants. Some short time after the rapid rise in diatoms and other plant organisms there is an associated rise in the number of mircoscopic animals, particularly copepods, and these form the main food materials of the smaller fish. In Norway the spring rise in the number of diatoms, and hence in copepods, attracts enormous shoals of small fish, chiefly capelan (*Mallotus vilosus*), to the northern coast (Finmarken), where they spawn. These shoals are followed by great numbers of cod, coal-fish, haddock, and other species which devour the capelan in enormous quantities. It is probable that the diatoms are the sole original source of vitamin A for fish, just as are green plants for land animals, as no case has yet been recorded in which this factor can be synthesised by the animal organism.

A further parallelism between land and sea animals is the provision made for the supply of vitamin A to the young. The ova of fish normally contain large amounts of this factor. During the subsequent development of the young larval fish the vitamin is in some way utilised so that at or shortly before the stage at which the contents of the yolk-sac are absorbed, the supplies of vitamin are almost exhausted. This appears to be one of the reasons why this stage is such a critical one in the development of, *e.g.*, trout in fish hatcheries.[14] [15]

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[11] *Biochem. J.*, 1922, **16**, 482; *J.*, 1922, 913A.

[12] *Ibid.*, 1921, **15**, 654.

[13] *Ibid.*, 1922, **16**, 518; *J.*, 1922, 913A.

The vitamin content of some Indian foodstuffs has been investigated by S. N. Ghose,[16] who has obtained indications that bleached flour is deficient in vitamin B as compared with unbleached flour. This is an important observation, and it is very desirable that investigation of this point should be extended to wheat flour as bleached in this country. It is known that the main effect of bleaching flour by means of nitrogen peroxide is the destruction of part of the carrotene and xanthophyll naturally present, to which the yellow colour of the flour is due. Although these pigments have not, in the pure state, any effect on growth, and have been shown not to be identical with the growth-promoting factors, yet it is undoubtedly the case that foodstuffs rich in carrotene are, more often than not, also rich in one or more of the accessory factors. It is by no means certain that there may not be some connexion between them as they exist in the foodstuff, and it is at least possible that a chemical agent which oxidises or otherwise destroys the natural pigment may, at the same time, destroy some of the accessory factors. If this be the case, the widespread practice of bleaching flour with nitrogen peroxide may have an effect on its nutritive value far more significant than the presence of traces of nitrites, or minute changes in the character of the proteins or fat.

CANNED FOODS.

The bacteriology of canned meat and fish is the subject of an important report by W. G. Savage, R. F. Hunwicke, and R. B. Calder.[17] These investigators lay stress on the fact that sterility is not, in itself, a reliable test of soundness, and that samples cannot be justifiably condemned merely because they are not sterile. Unsoundness in tins is usually the result not of bacteria gaining access from outside, but of the conditions within the tin having become changed (*e.g.*, by access of sterile air) in such a way as to enable bacteria already present to multiply and decompose the food.

Yeasts may cause unsoundness in products containing sugars, such as canned fruits and milk, but are of no importance in meat and fish products. Moulds are chiefly of interest as evidence of the access of air. Among the bacilli the obligate anaerobes, when found, were nearly always associated with active decomposition of the food. Sporing and non-sporing aerobic bacilli cause spoilage only in proportion as they possess proteolytic or fermentative abilities. It was observed that many aerobic sporing organisms can multiply under stringent anaerobic conditions, but not with sufficient freedom to produce proteolytic enzymes. Thermophilic bacteria, which have hitherto been very little studied, are widely present in canned foods, but are practically all non-proteolytic. No bacilli of the food-poisoning type were found in any of the products examined (116 tins of meat and 207 tins of various foodstuffs), nor was any evidence obtained that the organisms associated with the unsound conditions were pathogenic to man.

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[14] K. H. Coward and J. C. Drummond, *ibid.*, 1922, **16**, 631; *J.*, 1922, 993A.

[15] J. Hjort, *Proc. Roy. Soc.*, 1922, **B 93**, 440; *J.*, 1922, 564A.

[16] *Biochem. J.*, 1922, **16**, 35; *J.*, 1922, 343A.

[17] *Special Report No.* 11 *of Food Investigation Board*, Dept. of Scientific and Industrial Research, 1922.

A second report by W. G. Savage[18] on the methods used for the inspection of canned foods has been issued by the Department of Scientific and Industrial Research. This report, which deals with canned marine products, is on the same lines as the one on canned meats by the same author published in 1920, and referred to in detail in last year's Annual Reports (p. 485). Another publication on canned foods is in the form of a circular by W. D. Bigelow,[19] sent out by the research laboratory of the National Canners' Association, and dealing with springers and perforations in canned fruit. An interesting feature of these two reports is the discussion on the causes which lead to "springers," *i.e.*, cans which have lost their original vacuum without actually becoming blown, and the sides of which can be pressed in with the fingers and spring out again on releasing the pressure. Bigelow ascribes the loss of vacuum in the majority of cases to the production of hydrogen by the action of organic acids upon innumerable pinpoints on the inner surface of the can where the coating of tin is defective. Eventually this action may lead to actual leaks. Savage mentions that many cans showing a springy condition were carefully tested by the most reliable methods available, but no evidence of a leak was detected. In about 50% of springy tins the contents were sound and in these there was no evidence of any formation of gas by bacterial agency. He does not, however, refer to the possibility of hydrogen being produced by chemical action. In this connexion reference may be made to Serger's analyses of the gases found in blown cans, discussed in last year's Annual Report (p. 486). These were found to contain in a few cases as much as 60% of hydrogen, although carbon dioxide and nitrogen were usually predominant. It is not at all clear to what extent the taking up of tin by canned foods is accompanied by production of hydrogen, and the action of various foodstuffs on tin would seem to require further investigation on the purely chemical side.

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[18] *Special Report No.* 10 *of Food Investigation Board*, Dept. of Scientific and Industrial Research, 1922.

[19] *National Canners' Assoc. Research Laboratory Circular* 1-*L*, 1922.

One of the most interesting cases of food poisoning of recent years was the outbreak of botulism at Loch Maree, in Rossshire, last August, resulting in the death of eight persons. This was the first recorded case of poisoning by *Bacillus botulinus* in this country, although this type of food-poisoning has been recognised for nearly a century on the continent, where it is often spoken of as "sausage poisoning." In the United States, particularly on the Pacific Coast, it is comparatively common, and E. C. Dickson[20] considered that it is endemic in some parts of the States. The bacillus itself was first isolated by Van Ermengem in 1896. Botulinus poisoning is marked by an extremely high incidence of mortality—30–50%, or even higher—and the symptoms are quite distinctive, being characterised in the early stages by double vision, due to paralysis of the eye muscles, followed by progressive paralysis of the throat muscles, and eventually of the whole central nervous system. The bacillus is strictly anaerobic, and appears to be unable to develop in the animal body, the symptoms being due entirely to the extremely potent toxin previously produced in the foodstuff. The spores themselves, in moderate number, may be swallowed with impunity. Danger arises only when the number is so large that the toxin in the spores themselves is sufficient to produce symptoms, or when vegetative growth, with accompanying production of toxin, has commenced. According to Savage,[21] as little as 0·0003 to 0·001 c.c. of a broth culture, when injected into a rabbit, will kill it. Savage states that the majority of the American cases have been traced to home-canned vegetables or fruit, but outbreaks have frequently followed the consumption of smoked and tinned meat, raw and salted fish and other foodstuffs. In the Loch Maree cases the infection was traced to wild-duck paste, put up in small glass jars.

The manner in which this paste came to be infected with the bacillus is not clear. American investigators have shown that *Bacillus botulinus* is often found upon the surface of growing fruits and vegetables, bruised cherries, decaying leaves, and the bodies of insects, and that its spores are fairly widely distributed through the soil of the Western States. Both the bacillus and its toxin appear to be easily destroyed by heating to 70°–80° C. The spores, which are readily formed under suitable conditions, are far more resistant to heat, it being stated that exposure to a temperature of 100° C. for 5 hrs., 105° for 40 mins., or 120° for 6 mins. is required to kill them. The United States Department of Agriculture states that they are killed in 1–4 hrs. at 100° C. At the enquiry at Dingwall evidence was given to the effect that the wild-duck paste in question had been processed at a temperature of 102° C. for

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[20] "Botulism," Monograph of the Rockefeller Institute of Medical Research, New York, 1918.

[21] "Food Poisoning and Food Infections," Cambridge, 1920.

50 mins. In this connexion reference may be made to the work of G. E. Thompson in 1919,[22] and W. D. Bigelow in 1920, on the rate of heat penetration in processing canned foods, to which detailed reference was made in last year's Report (p. 484), and which showed how extremely slowly heat penetrates to the centre of a can, if the foodstuff be in a pulpy or finely-divided state.

It does not, however, follow that the presence of living spores in canned food will necessarily give rise to dangerous amounts of the toxin. The conditions as regards temperature, acidity or alkalinity, nature of the foodstuff, etc. may not be favourable to the vegetative growth of the spores, and it is possible that the conditions necessary for this particular bacillus are somewhat sharply defined, and are but rarely present.

One possible safeguard against the consumption of food dangerously contaminated with *Bacillus botulinus* is the pronounced odour of butyric acid which is produced, but with highly-seasoned products this indication may easily be masked. A further safeguard is the fact that this bacillus is a gas-producing organism when glucose is present, and should cause blowing of the tin if it multiplies in canned fruit.[23]

An interesting aspect of the matter is the possible relationship of *Bacillus botulinus* to the so-called "limberneck" disease of chickens, and to "fodder" or "grass disease" in horses. It appears that more than one type of *Bacillus botulinus* may exist. Type A is responsible for food poisoning in man, and also, apparently, for the disease in chickens, but it is not clear to what extent the type B bacillus, which is alleged to be responsible for grass sickness in horses, is concerned in food poisoning cases. It is perhaps no more than a coincidence that grass sickness should be prevalent in certain parts of Scotland, having been first investigated by a special Committee of the Highland and Agricultural Society of Scotland in 1918.[24]

A useful paper by R. E. Essery[25] draws attention to the value of fish scales as a means of identification of the fish used in manufactured products. Diagrams are given which show that the typical scales of various fish are widely different in appearance and are quite characteristic of the individual.

C. S. Purcell and C. H. Hickey[26] have noted the occurrence of well-defined crystals of struvite (magnesium ammonium phosphate $MgNH_4PO_4,6H_2O$) in canned shrimps. The presence of this compound in foodstuffs appears to be very unusual, and would seem to indicate that the foodstuff must have become strongly ammoniacal through decomposition. Whether or not the shrimps in question were in a sound condition is not stated.

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[22] *J. Ind. Eng. Chem.*, 1919, **11**, 657.
[23] W. G. Savage, *The Medical Officer*, July 15, 1922.
[24] *Veterinary J.*, 1922, **78**, 125.
[25] *Analyst*, 1922, **47**, 163; *J.*, 1922, 387A.
[26] *Ibid.*, 1922, **47**, 16.

STORAGE OF FRUIT.

A long *résumé* of work carried out on the storage of apples is given in the Annual Report of the Food Investigation Board for the year 1921. The enquiry is being carried out along three main lines: the preservation of fruit by cold or by "gas" storage, the chemistry of the process of ripening, and the diseases of fruit when stored. It is concluded that a temperature of 1° C. is most satisfactory for the cold storage of apples, and that of apples grown on different soils, those from silt have the best keeping properties, while those from open clay and fenland are the least adapted for long storage. In clay soil, the fruit from trees grown on grass land was superior in keeping qualities to that grown on open ground. A sharp distinction is drawn between loss due to physiological disease such as "scald" and that due to mould. At 1° C. the loss is almost entirely due to disease, moulds being unable to develop actively until a temperature of 3°–5° C. is reached. Further factors which may influence the keeping qualities of apples in cold storage are the age of the tree, the size of the fruit, and the degree of maturity when placed in cold store, and these factors are being investigated.

Apple "scald" is a brown disfiguring mark on the skin of the apple. It is at first confined to the skin, and usually appears in the first instance on the green side of the apple, but affected areas become readily infected with mould, which soon causes destruction of the apple. It appears that artificial "scald" can be produced on apples by the vapours of ethyl acetate and amyl acetate, and it is possible that these and similar odorous constituents given off by apples during storage may be a contributory cause of "scald." American investigators have found that scald may be completely prevented by wrapping the apples in materials impregnated with an odourless mineral oil, which apparently acts as an absorbent for odorous constituents, and this has been confirmed by experiments carried out in this country.

The gas storage of fruit is the subject of another patent taken out by the Imperial Trust for Encouragement of Scientific and Industrial Research.[27] The claim is made for the storage of fruit in an artificial atmosphere containing up to 20% of oxygen and 20% of carbon dioxide, the atmosphere being saturated up to 70–90% with water vapour.

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[27] E.P. 172,673 *J.*, 1922, 115A.

M. H. Carré and D. Haynes[28] discuss the conditions under which pectin is hydrolysed by sodium hydroxide, and show that if the hydrolysis be carried out under certain conditions and the solution subsequently treated with acetic acid and calcium chloride, calcium pectate is precipitated quantitatively in a form which is easily washed and dried. Test analyses indicate that the method is accurate. The weight of calcium pectate obtained from 100 g. of apples is about 0·5 g. It has been found that the soluble pectin of stored apples reaches a maximum and then declines. Full ripeness is reached slightly before the stage of maximum pectin content, and over-ripeness and rapid break-up of the fruit coincides with a decrease in pectin content.

MILK AND DAIRY PRODUCTS.

A great deal of work has been done in recent years in connexion with the pasteurisation of milk, a subject which is now very much to the fore, in view of legislative enactments either already in force or proposed. In the pasteurisation of milk we may distinguish two chief methods, the "flash" process and the "holding" process. In the former the milk flows in a continuous stream through a system in which it is rapidly heated to about 175° F. (80° C.), and almost immediately cooled. The milk is exposed to this temperature for a very short time, not more than thirty seconds or a minute. In the holding process the milk is heated to a lower temperature, 145° F. (63° C.), but is retained at this temperature for about half-an-hour. In last year's report (p. 482) the relationship between temperature and time necessary to kill any given type of micro-organism was illustrated by some results obtained by Bigelow for canned foods, and the same kind of relationships hold good in the pasteurisation of milk. The lower the temperature the longer the time required to effect efficient pasteurisation. In the case of milk it is of the greatest importance that the taste and other characteristics, such as the rising of the cream, be not adversely affected, and that the accessory nutritive factors, which are sensitive to heat and oxidation, be not destroyed. Opinion in this country definitely favours the holding process as being the more efficient, and the less likely to damage the milk from the nutritive standpoint. Most of the holding processes hitherto in use, however, do not allow of a continuous flow through the apparatus, and this is a great disadvantage when large quantities of milk have to be dealt with expeditiously. Attempts have been made to overcome this by the use of so-called "flow-holders," in which the milk flows continuously through a heater of such a size that the milk stream takes about half-an-hour to pass from the inlet to the outlet. It is, however, almost impossible to ensure that each particle of milk will remain for the same time in the heater. Owing to convection and eddy currents some of the milk will pass through very much too quickly, while there will always be a residue in some corner of the vessel which may remain there for much longer than half-an-hour. This effect can readily be demonstrated by adding a dye to the milk at the inlet, and observing how long it takes for traces of the dyed milk to reach the outlet. If the holder be designed to hold the milk for half-an-hour and the dye appears at the outlet in 7½ mins., the holder may be said to have an efficiency of 25%.

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[28] *Biochem. J.*, 1922, **16**, 60; *J.*, 1922, 342A.

Many flow-holders now on the market have efficiencies as low as 10 or 15%, and it is rare to find one as high as 30%. Moreover, it is not by any means certain that a full-sized plant will show the same efficiency as a small-scale model. If a sufficient number of baffles were introduced the efficiency could, of course, be greatly raised (a flow holder filled with shot or glass marbles would probably have an efficiency of 100%), but the practical impossibility of keeping such a vessel clean prohibits its use in actual practice. With absolute or "positive" holding processes, apart from the difficulty of providing for a continuous flow, leakage through the outlet cock has hitherto given rise to much trouble. After prolonged use almost every type of cock is liable to leak, with the result that a minute quantity of practically raw milk is constantly passing through into the finished product. These defects, however, would appear to have been overcome in recent models. The diagrams below indicate the principles upon which some of these forms of positive holder are constructed.

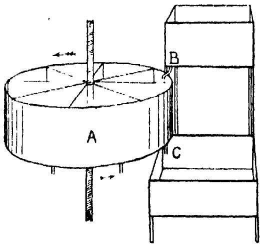

FIG. 1.

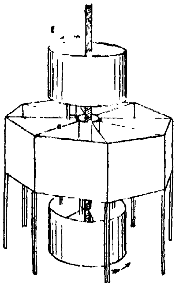

FIG. 2.

The circular vessel, A, (Fig. 1), rotates slowly upon its vertical axis, taking approximately half-an-hour to make a complete revolution. It is divided into compartments which are filled automatically as they come in turn under the inlet pipe, B, with milk previously heated to the required temperature. Each compartment is provided with an outlet which remains closed until the rotation of the vessel brings the compartment in question directly over the fixed receiver, C, when the outlet cock is automatically opened and the contents discharged. The process is thus continuous and any leakage from the outlet cocks during the holding of the milk flows down a separate channel, and not into the final receiver.

Figure 2 shows a second form in which the compartment vessel is stationary while the inlet pipe and the receiver for the pasteurised milk rotate slowly round the vertical axis. As the receiver comes into position below each compartment the outlet cock is opened automatically, and subsequently closed.

An interesting form of pasteuriser has been developed in Denmark, in which the milk is passed through a system of tube under a pressure of 90 lb. per sq. inch and heated to a temperature of 275° F. (135° C.) for a period of about 45 secs. The apparatus is, in effect, a flash steriliser, all micro-organisms being completely destroyed by the high temperature employed, but it is claimed that the complete absence of air during heating prevents the milk from acquiring a burnt taste, and that the destruction of accessory factors by oxidation is avoided. Milk sterilised by this process and introduced under sterile conditions into specially constructed churns has been shipped to this country from South Africa, and has arrived in perfectly good condition, being hardly distinguishable from fresh milk. The process does impart to the milk a very slight " biscuity " flavour, but this is in no way comparable to the pronounced burnt taste of boiled milk. It is not clear whether the small amount of dissolved oxygen, of the order of about 10 c.c. per litre, which is always present in fresh milk, and which gradually diminishes on keeping with production of carbon dioxide through bacterial action, is removed from the milk prior to sterilisation. Unless this be done it would seem that some oxidation must occur during the process. One patent has for its object the withdrawal of dissolved gases by subjecting the milk to sub-normal pressure previous to pasteurisation.[29]

A novel method of preserving milk is the subject of an American patent.[30] Fresh milk is agitated under a partial vacuum at approximately the same temperature as that which it possesses at the moment of milking, and is then charged with carbon dioxide and filled into containers at a temperature of 40° F. (5° C.) under a pressure of 60 lb. per sq. in.

A long paper by A. F. Weinlig [31] discusses the changes taking place in milk on pasteurisation at various temperatures under laboratory conditions, mainly in regard to the rising of the cream, the coagulation of albumin and the alteration in the casein due to the partial precipitation of calcium and magnesium salts.

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[29] A. Jensen, U.S.P. 1,396,632 ; *J.*, 1922, 30A.

[30] C. L. Arnoldi, U.S.P. 1,403,223 ; *J.*, 1922, 154A.

[31] *Forsch. Geb. Milchwirtsch. u. Molkereiwiss.*, 1922, **2**, 127, 175 ; *J.*, 1922, 833A.

The non-protein nitrogenous substances in milk are the subject of two papers,[32] in which it is shown that milk contains lysine, arginine, histidine, guanine, adenine, choline, creatine, creatinine, uric acid, and urea. The concentration of these in the blood seems to control the amount secreted in the urine, and also the quantity present in the milk, the mammary gland acting to some extent as an excretory organ for the waste non-protein nitrogenous substances in the blood.

A paper by G. Viale and A. Rabbeno[33] on the chemical changes occurring in condensed milk on keeping is of interest in view of the attention now being paid to the question of standards for condensed milk and methods of analysis of the sweetened product. They find that, in general, the acidity increases on keeping, but is subject to considerable variations. This increase of acidity brings about a slow hydrolysis of the proteins, and polypeptides, which are absent in fresh milk, show a marked increase on storage. A partial hydrolysis of disaccharide also takes place, some of the older samples showing a decrease in lactose to half the original figure, and a decrease in sucrose to about 15%. The fat content in fresh samples was 8·6%, and fell after keeping for several years to 3·4%. These observations refer to milk which had been kept for periods of from ½ to 8 years, and which had in many cases become brown, owing to oxidation of acids or decomposition of sugars. It is not likely that such extensive changes would be observed in the ordinary condensed milk of commerce, but the fact that they are liable to occur should be borne in mind when examining these products.

Increased attention is being directed to the utilisation of whey,[34] and one patentee proposes to treat whey with lime below 70° C. to form the calcium compound of lactose, which is subsequently treated with carbon dioxide or sulphur dioxide, and the clear liquor evaporated until crystallisation commences.[35] D. Thomson[36] proposes to reduce the acidity of whey in stages by successive additions of alkali, the protein precipitated at each stage being filtered off, washed, and dried. The addition of alkali is continued until the reaction of the liquid corresponds to $p_H = 10{\cdot}5$, *i.e.*, well on the alkaline side. On evaporation of the solution the whole of the remaining protein coagulates and the lactose is recovered from the clear filtrate by crystallisation. One of the chief difficulties in the preparation of lactose from whey appears to lie in the comparatively large quantity of uncrystallisable molasses produced. Hitherto it has not been easy either to find profitable outlets for this molasses, or to extract from it a further quantity of lactose.

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[32] Y. Hijikata, *J. Biol. Chem.*, 1922, **51**, 165; *J.*, 1922, 341A. W. Taylor, *Biochem. J.*, 1922, **16**, 611; *J.*, 1922, 993A.

[33] *Biochem. Terap. Sperim.*, 1921, **8**, 325; *J.*, 1922, 725A.

[34] *Ann. Repts.*, 1921, **6**, 493.

[35] B. Bleyer, G.P. 341,787; *J.*, 1922, 71A.

[36] D. Thomson, E.P. 173,831; *J.*, 1922, 192A; U.S.P. 1,428,820 1922, 834A. *Cf.* also Metallbank u. Metallurgische Ges., G.P. 344,450 1922, 192A.

ANALYTICAL AND MISCELLANEOUS.

The accurate estimation of starch in foodstuffs is a matter of some difficulty. Practically all the methods in use depend either upon the measurement of the optical rotation, or upon the cupric reducing power, of the conversion products obtained by the action of acids or of diastase upon the starch. The difficulty with all these methods is that other optically active and, under some conditions, reducing substances besides starch conversion products usually pass into solution, this being specially the case when acids are used as converting agents. A. R. Ling[37] has commenced a comprehensive investigation on this subject, starting from the observations of Brown and Morris[38] that when starch is hydrolysed by malt diastase at 55°–60° C. there is a resting stage which, when the hydrolytic change is followed by the rotatory and reducing powers of the products, is found to be in accordance with the empirical equation :—

$$10C_{12}H_{20}O_{10}+8H_2O=\underset{\text{Maltose.}}{8C_{12}H_{22}O_{11}}+\underset{\text{Dextrin.}}{2C_{12}H_{20}O_{10}}$$

According to this equation 100 parts of starch should yield 84·4 parts of maltose. It is found, however, that the actual percentage of maltose, as determined by the cupric-reducing power of the mixed products, depends on the diastatic power of the malt employed. Thus with a malt of 80° Lintner the apparent maltose is 84·4% of the starch, while with a malt of diastatic power 40° Lintner it is 82·5%.

Ling has worked out the relationship between the diastatic power of the malt and the percentage of apparent maltose found by cupric reduction, and the results show that starch may be estimated by this method in barley and wheat with a high degree of accuracy. Sugars, fats, and alcohol-soluble proteins are removed from the finely-ground grain before conversion by extraction with alcohol of sp. gr. 0·920, according to O'Sullivan's original method.

The detection and determination of added sulphites or sulphur dioxide in foods is always a matter of difficulty. On distillation in presence of phosphoric acid volatile sulphur compounds other than sulphur dioxide pass over into the distillate, and are oxidised to sulphuric acid by bromine water. It is usual to make some allowances for the sulphuric acid thus formed, but the error involved may be great, especially in the case of foodstuffs flavoured with onions or containing mustard. E. F. Kohman[39] shows that hydrogen sulphide is evolved from many foodstuffs on cooking, and may be estimated as sulphuric acid in the distillate by oxidation with bromine water. A. C. Chapman[40] finds that if the distillate be collected in hydrogen peroxide instead of bromine water, volatile sulphur compounds other than sulphur dioxide are not oxidised to sulphuric acid, and that provided that the quantity of sulphur dioxide be not great, a fairly good differentiation may be obtained by this method.

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[37] *J. Inst. Brewing*, 1922, **28**, 838; *J.*, 1923, 48T.

[38] *Chem. Soc. Trans.*, 1885, **47**, 527.

O. Köpke and E. Bodländer[41] give a method for the determination of benzoic acid in margarine, in which the sodium bicarbonate extract before acidification is treated with ammonium sulphate, which precipitates proteins. It is claimed that the ammonium sulphate prevents the formation of the troublesome emulsion which often occurs on subsequent extraction with ether.

Two new methods of determining boric acid in foodstuffs are worthy of attention. Thomson's method, with its various modifications, is liable to yield low results in presence of much phosphoric acid, owing to the tendency for calcium borate to be precipitated if the solution be allowed to become too alkaline. W. M. Deerns[42] gives a method for determining boric acid in shrimps, which would seem to be applicable to other foodstuffs. The essential feature is the removal of phosphoric acid by the addition of ferric chloride, and subsequent neutralisation with calcium carbonate. I. M. Kolthoff[43] finds that the addition of sodium citrate to solutions containing phosphoric and boric acids prevents interference by the latter in the titration of the phosphoric acid with sodium hydroxide. After neutralisation addition of mannitol allows of the titration of the boric acid by further addition of sodium hydroxide until neutral to phenolphthalein.

L. Singh[44] has studied the effect of acidity in promoting the "jellying" of fruit juice. The higher the acidity the less the quantity of sugar required to cause the juice to set. Thus, an increase from 0·05% to 2·05% of organic acids reduces the amount of sugar required by over 30%.

According to a patent by F. G. Beylik and N. W. Schwartzlose[45] a crude mixture of pectous materials is prepared from plants by dehydrating at a low temperature, and extracting the greater part of the non-pectous materials with alcohol. The residue consists largely of pectin, pectic acid ($C_{16}H_{22}O_{15}$) and pectosic acid ($C_{32}H_{46}O_{31}$) together with cellular tissue, and when added in small quantities to fruit juices will produce a clear jelly.

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[39] *J. Ind. Eng. Chem.*, 1922, **14**, 527 ; *J.*, 1922, 780A.

[40] *Analyst*, 1922, **47**, 204 ; *J.*, 1922, 515A.

[41] *Z. Unters. Nahr. Genussm.*, 1922, **43**, 345 ; *J.*, 1922, 644A.

[42] *Chem. Weekblad*, 1922, **19**, 397, 480 ; *J.*, 1922, 873A, 1001A.

[43] *Ibid.*, 1922, **19**, 449 ; *J.*, 1922, 963A.

19. [44] *J. Ind. Eng. Chem.*, 1922, **14**, 710 ; *J.*, 1922, 726A.

1922 E.P. 184,081 ; *J.*, 1922, 781A.

C. F. Muttelet[46] proposes to detect the presence of apple juice in certain mixed jams by determining the relative proportions of malic and citric acids present. The acidity of red and black currants, raspberries, and strawberries is due to the presence of citric acid, that of apples, pears, and cherries being due to malic acid. This agrees with the results obtained by W. D. Bigelow and P. B. Dunbar in 1917,[47] who, however, found that currants and raspberries may contain traces of malic acid, while in some varieties of pears citric acid predominates over malic acid. H. Franzen and F. Helwert[48] also find that malic acid is the most important acid in cherries, although small quantities of other acids are present. The method of estimation employed by Muttelet depends upon the isolation of barium malate and citrate by precipitation in 80% alcohol, dissolving the mixed precipitate in water, and precipitating the barium citrate by adding alcohol until the liquid contains 33%. Barium malate remains in solution, and is subsequently precipitated by raising the alcohol content of the liquid to 66%. Apple and quince jellies examined by this method yielded 0·172–0·310% of malic acid, but the presence of this acid was not detected in currant and raspberry jams.

In an interesting article on the comparative sweetness of cane and beet sugars, J. P. Ogilvie points out that refined sugars, from whatever source obtained, are indistinguishable as regards sweetness and suitability for all purposes.[49] These refined products contain on the average about 99·95% of sucrose. The lower grades, or direct-consumption sugars, contain about 99·5% of sucrose and their sweetness may be affected by the slight traces of acid or alkaline impurities which they contain. There appears to be reliable evidence that the intensity of sweetness as registered by one set of nerves in the palate may be modified when another set of nerves, *e.g.*, those registering an acid or an alkaline taste, is at the same time excited. Sugar appears to be sweeter when traces of fruit acids are present than when, as is the case with beet sugar, traces of alkalis are present.

The use of hypochlorites or of electrolysed salt solutions for food preservation appears to be on the increase. Among several recent patents dealing with this subject is one in which it is proposed

[46] *Ann. Falsif.*, 1922, **15**, 196 ; *J.*, 1922, 726A.
[47] *J. Ind. Eng. Chem.*, 1917, **9**, 762.
[48] *Z. physiol. Chem.*, 1922, **122**, 46 ; *J.*, 1922, 875A.
[49] *J.*, 1922, 343R.

that ice used for preserving fish should be made from water which has previously been treated with a hypochlorite.[50]

A new preservative for foodstuffs has been found in nitrous oxide.[51] This gas when dry exerts no bactericidal action, but the moist gas at increased pressure kills all vegetative forms of bacteria, but not spores or conidia. It is stated that milk treated with nitrous oxide at 30 to 35 atmospheres pressure can be preserved for a month, even at 18°–37° C. The original properties of the milk are fully retained after treatment with nitrous oxide. Meat can be kept for a month after treatment with the gas at 38 atmospheres pressure. The extremely high pressures which are necessary would seem to militate against the commercial development of this process.

In view of recent developments in the use of hydrocyanic acid gas for the fumigation of ships, the extent to which the gas is absorbed by foodstuffs, grain, etc. may become a question of importance. It would be of great advantage if it were possible to fumigate a ship for the destruction of rats and other vermin before discharge of the cargo, without damaging or contaminating foodstuffs. According to experiments carried out in Italy, hydrocyanic acid is not absorbed by foodstuffs except in negligible traces, but it is usually the practice in this country to remove them prior to fumigation. In Holland fumigation is being carried out by "Cyclon" (methyl cyanoformate $CN{\cdot}COOCH_3$), in place of hydrocyanic acid, and the extent to which this substance is absorbed by foodstuffs has been investigated by J. D. Jansen, W. Schut, and M. Wagenaar.[52] They find that meat and water absorbed up to 700 mg. of HCN per kg., while in dry foods such as coffee, mustard, etc. hydrocyanic acid could not be detected. Presumably the absorption by meat was confined to the portions close to the surface. It would appear unlikely that hydrocyanic acid in the concentration employed (1 part in 500–1000 pts. of air) would be capable of contaminating foodstuffs to a dangerous extent.

A novel application of hydrogenation, and one which illustrates the continued search in Germany for substitutes for all manner of foodstuffs, is to be found in a patent for the production from fish roes of a substitute for eggs.[53] The solution obtained by extracting fish roes with a solvent for lecithin, *e.g.*, alcohol or ether, is hydrogenated, after removal of a portion of the solvent, until the product has an odour similar to that of egg yolk. The remainder of the solvent is separated and the product is mixed with material containing protein, *e.g.*, the extracted fish roe residues.

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[50] W. E. Gibbs, E.P. 185,986 ; *J.*, 1922, 873A.

[51] H. Bart, *Arch. Hyg.*, 1922, **91**, 1 ; *J.*, 1922, 725A.

[52] *Chem. Weekblad*, 1922, **19**, 373 ; *J.*, 1922, 873A.

[53] G.P. 342,308 ; *J.*, 1922, 115A.

G. Bertrand and M. Mokragnatz[54] find that nickel is present in practically all vegetable foodstuffs, while cobalt is absent only from carrots and oats. The quantity of nickel varied from 0·01 mg. to 2 mg. per kg. of the fresh substance, and of cobalt from 0·005 mg. to 0·3 mg.

The significance of traces of manganese in marine organisms, referred to in last year's Annual Report, is dealt with by C. Berkeley.[55] He considers that in marine worms there is no evidence that the presence of manganese is associated with any physiological function such as respiration.

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[54] *Comptes rend.*, 1922, **175**, 458 ; *J.*, 1922, 873

[55] *Biochem. J.*, 1922, **16**, 70.

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SANITATION AND WATER PURIFICATION.

By H. T. Calvert, M.B.E., D.Sc., Ph.D., F.I.C.,

Chemical Inspector, Ministry of Health, London.

During the year under review several economic factors have operated in such a way as to result in considerable activity in the construction of sewage disposal works and works of water supply. The problem of unemployment has been and still is very serious, and Local Authorities have been urged by the Government to formulate schemes for its relief. State financial assistance, either in the form of a grant towards the labour charges or in the form of a payment of a proportion of the total annual charges in respect of such schemes, has been available for work which has been undertaken at an earlier date than it otherwise would have been had it not been for the acute unemployment prevailing. In addition, the very limited expenditure incurred on schemes of sewage disposal and water supply during the past few years has resulted in the necessity for making up considerable lee-way in order to maintain works in a moderate state of efficiency. The drought of 1921 also taught its lesson to some extent, and many Local Authorities and Water Companies have, as a result, carried out extensions to their waterworks in order to be forearmed against a recurrence of the drought. The lesson of the 1921 drought has perhaps not been fully appreciated because the year 1922 has been one of trade depression; had it been a year of trade boom manufacturers would have required much larger volumes of water for trade purposes, and several authorities would have been hard pressed to meet these requirements.

The scientific work which has been accomplished during the year may perhaps be better characterised as isolated patches of research work than as a united attack on the problems which present themselves, and in view of the enormous expenditure which the country incurs every year in providing a water supply and in disposing of the resulting sewage, the time cannot be long delayed when either some Pasteur will arise or some Central Government Department be established as a result of whose scientific investigations[1] not only will this enormous expenditure be reduced, but there will accrue considerable benefit to the public health of the country.

As an indication of the magnitude of this expenditure it may be stated that at the end of the financial year 1919–1920, the latest year for which returns[2] are available, the outstanding debt of Local Authorities in England and Wales in respect of works of sewerage and sewage disposal was £39,000,000, and that in the same year an expenditure of £7,000,000 was incurred on these works in meeting loan charges and maintenance costs. Owing to economic conditions the present-day figures are no doubt somewhat larger.

SANITATION.

Under this heading it is proposed to refer to the treatment of sewage and liquid trade refuse, the prevention of river pollution, and the disposal of towns' solid refuse.

Sewage.

During the past few years the activated sludge or bio-aeration process of sewage treatment has received an increasing amount of attention, and Local Authorities have felt compelled to examine the possibilities of this process, and of its applicability to their local conditions, before embarking on expenditure for the construction of new sewage disposal works, or even for the extension of existing works. This has led to a wider application of the process, and several towns in Great Britain are at the present time constructing works on these lines. In America, more especially in the case of the communities on the shores of the Great Lakes, large schemes of sewage disposal are in hand, and it is noteworthy that in many of these cases the activated sludge process has been adopted. It should be pointed out, however, that in these cases it has been a question of entirely new works and not, as is now often the case in Great Britain, a question of extending existing works. Hitherto, these American communities have discharged their crude sewage into and derived their water supplies from the Great Lakes, and have relied upon dilution as a first stage in the purification. There have been indications that in view of increasing populations such dilution can no longer be relied upon, and there are at present in these American communities two schools, the one advocating purification of the sewage before its discharge, and the other advocating a strengthening up of the water treatment works. There can be no doubt that ultimately both schools will have their way.

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[1] *Mun. Eng. and San. Rec.*, March 2, 1922, 203, 204.

[2] *Ministry of Health, Annual Report*, 1921-1922.

Dilution as a method of sewage disposal was advocated by the Royal Commission on Sewage Disposal, 1898, in their Eighth Report[3] in 1914, but since that date an insufficient amount of attention has been paid to the subject. G. B. Kershaw,[4] in a paper read before the Institution of Sanitary Engineers, dealt with the matter, and F. W. Wells[5] has recently attempted to define the dilution necessary to attain the standard of a drinking water. He regards as the unit concentration of extreme contamination the daily wastes of one person in one gallon; one hundred times this dilution yields average American sewage, and one million times an average drinking water, whilst one hundred million times would yield a water which would pass the most stringent tests which could be applied to a water supply. Like the Royal Commission on Rivers Pollution Prevention of 1868, Wells fails to allow for the variations in the biological activity of the diluting water, but as a scientific study breaking new ground the work is very useful. From practical experience R. Hering[6] came to the conclusion that a dilution of 2½ to 5 cubic feet per second was necessary to prevent a nuisance in dealing with the sewage of a population of 1000.

Perhaps the most striking application of the dilution method is the pumping of water from Lake Michigan to dilute the sewage of one district of Chicago before its discharge into the Mississippi valley. This action enabled the City of Chicago to avoid to some extent the discharge of its sewage in close proximity to its water intake, but the limitation placed by the U.S. War Department, acting in the interests of the navigation of the Great Lakes, and by the Courts, on the amount of water which may be thus diverted from its natural course, has made it necessary to take further steps for the purification of the sewage of the Northern District of Chicago. A further application of the principle involved in purification by dilution is to be found in the arrangements[7] which have been made between the officials of the States of New Jersey and Pennsylvania, whereby the standards to be attained by the effluents from sewage works on the Delaware River will be varied in the different reaches of the river according to the volume of diluting water available. Dilution is, of course, only one of the many factors which should be taken into consideration in fixing a standard with which any sewage works effluent should comply.

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[3] *Eighth Report*, 1912. *Cd.* 6464. H.M. Stationery Office.

[4] *Surveyor*, May 5, 1922, 367.

[5] *Mun. Eng. and San. Rec.*, Oct. 19, 1922, 438.

[6] *Proc. Amer. Soc. Civ. Eng.*, 1922, **48**, 113.

[7] *Eng. News Rec.*, Aug. 10, 1922, 217, 243.

With regard to the treatment of sewage on land, where this has been combined with farming operations, the results from a financial point of view have been generally unsatisfactory during the year, and there has been a tendency to realise that the cropping or over-cropping of the land results in large areas being unusable at certain periods for the purification of sewage, so that the purification suffers. The cultivation of willows[8] on sewage farms has been urged as a rural industry, and the Ministry of Agriculture and Fisheries have issued a second edition of their pamphlet on the cultivation of osiers and willows.[9]

K. Imhoff[10] has proposed the use of shallow under-drained settling basins of a depth of 4 to 12 inches for the removal and subsequent drainage of the suspended matters in sewage. The under-drains are closed, and the sewage is allowed to enter the first of a series of such basins. When this is full of sludge, the inflow is stopped and the sewage is diverted into a second basin. The under-drains of the first basin are then opened, and the sludge drains to a sufficient extent to become spadeable. The process has been adopted in Germany at some sewage works, and also for the settlement of coal washing waters. It must be regarded as an economical measure to combine the advantages of well-constructed sedimentation tanks and sludge-drying beds.

The Prussian Minister of Public Welfare issued a decree[11] on June 30th, 1922, indicating to Local Authorities the principles which should underlie the disposal of sewage of new housing sites.

With regard to the treatment of sewage on artificial biological filters the question of the most suitable depth of the filters, which was inadequately considered by the Royal Commission on Sewage Disposal, has been reopened during the year and the results of experiments on the subject are expected shortly. The cultivation of *Achorutes viaticus* has been taken up at Glasgow by F. W. Harris[12] as a means of keeping the sewage filters clean and preventing them from becoming sludged up and impervious.

During the past few years a good deal of attention has been devoted in America to the electrolytic[13] or "direct oxidation" process for the treatment of sewage. From time to time since

[8] *Mun. Eng. and San. Rec.*, Nov. 2, 1922, 499; Nov. 16, 1922, 553; Nov. 30, 1922, 614; Dec. 7, 1922, 641.

[9] *Miscellaneous Publications No.* 18. H.M. Stationery Office.

[10] E.P. 184,742; *J.*, 1922, 696A.

[11] *Gesundheits-Ingenieur*, 1922, **44**, 611.

[12] *Mun. Eng. and San. Rec.*, Oct. 5, 1922, 392.

[13] *The American City*, 1922, **26**, 111.

purification of the sewage before its discharge, and the othe advocating a strengthening up of the water treatment works There can be no doubt that ultimately both schools will hav their way.

Dilution as a method of sewage disposal was advocated by th Royal Commission on Sewage Disposal, 1898, in their Eight Report[3] in 1914, but since that date an insufficient amount o attention has been paid to the subject. G. B. Kershaw,[4] in a pape read before the Institution of Sanitary Engineers, dealt with th matter, and F. W. Wells[5] has recently attempted to define th dilution necessary to attain the standard of a drinking water. H regards as the unit concentration of extreme contamination th daily wastes of one person in one gallon; one hundred times thi dilution yields average American sewage, and one million times a average drinking water, whilst one hundred million times woul yield a water which would pass the most stringent tests whic could be applied to a water supply. Like the Royal Commissio on Rivers Pollution Prevention of 1868, Wells fails to allow for th variations in the biological activity of the diluting water, but as scientific study breaking new ground the work is very useful. Fro practical experience R. Hering[6] came to the conclusion that dilution of 2½ to 5 cubic feet per second was necessary to preven a nuisance in dealing with the sewage of a populatio of 1000.

Perhaps the most striking application of the dilution method i the pumping of water from Lake Michigan to dilute the sewage o one district of Chicago before its discharge into the Mississipp valley. This action enabled the City of Chicago to avoid to som extent the discharge of its sewage in close proximity to its wate intake, but the limitation placed by the U.S. War Department acting in the interests of the navigation of the Great Lakes, and b the Courts, on the amount of water which may be thus diverted fro its natural course, has made it necessary to take further steps fo the purification of the sewage of the Northern District of Chicago A further application of the principle involved in purification b dilution is to be found in the arrangements[7] which have been mad between the officials of the States of New Jersey and Pennsylvania whereby the standards to be attained by the effluents from sewag works on the Delaware River will be varied in the different reache of the river according to the volume of diluting water availabl Dilution is, of course, only one of the many factors which shoul be taken into consideration in fixing a standard with which any sewage works effluent should comply.

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[3] *Eighth Report*, 1912. *Cd.* 6464. H.M. Stationery Office.

[4] *Surveyor*, May 5, 1922, 367.

[5] *Mun. Eng. and San. Rec.*, Oct. 19, 1922, 438.

[6] *Proc. Amer. Soc. Civ. Eng.*, 1922, **48**, 113.

[7] *Eng. News Rec.*, Aug. 10, 1922, 217, 243.

With regard to the treatment of sewage on land, where this has been combined with farming operations, the results from a financial point of view have been generally unsatisfactory during the year, and there has been a tendency to realise that the cropping or over-cropping of the land results in large areas being unusable at certain periods for the purification of sewage, so that the purification suffers. The cultivation of willows[8] on sewage farms has been urged as a rural industry, and the Ministry of Agriculture and Fisheries have issued a second edition of their pamphlet on the cultivation of osiers and willows.[9]

K. Imhoff[10] has proposed the use of shallow under-drained settling basins of a depth of 4 to 12 inches for the removal and subsequent drainage of the suspended matters in sewage. The under-drains are closed, and the sewage is allowed to enter the first of a series of such basins. When this is full of sludge, the inflow is stopped and the sewage is diverted into a second basin. The under-drains of the first basin are then opened, and the sludge drains to a sufficient extent to become spadeable. The process has been adopted in Germany at some sewage works, and also for the settlement of coal washing waters. It must be regarded as an economical measure to combine the advantages of well-constructed sedimentation tanks and sludge-drying beds.

The Prussian Minister of Public Welfare issued a decree[11] on June 30th, 1922, indicating to Local Authorities the principles which should underlie the disposal of sewage of new housing sites.

With regard to the treatment of sewage on artificial biological filters the question of the most suitable depth of the filters, which was inadequately considered by the Royal Commission on Sewage Disposal, has been reopened during the year and the results of experiments on the subject are expected shortly. The cultivation of *Achorutes viaticus* has been taken up at Glasgow by F. W. Harris[12] as a means of keeping the sewage filters clean and preventing them from becoming sludged up and impervious.

During the past few years a good deal of attention has been devoted in America to the electrolytic[13] or "direct oxidation" process for the treatment of sewage. From time to time since

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[8] *Mun. Eng. and San. Rec.*, Nov. 2, 1922, 499; Nov. 16, 1922, 553; Nov. 30, 1922, 614; Dec. 7, 1922, 641.

[9] *Miscellaneous Publications No.* 18. H.M. Stationery Office.

[10] E.P. 184,742; *J.*, 1922, 696A.

[11] *Gesundheits-Ingenieur*, 1922, **44**, 611.

[12] *Mun. Eng. and San. Rec.*, Oct. 5, 1922, 392.

[13] *The American City*, 1922, **26**, 111.

Kirkham in 1870 suggested electrolysis as a method of oxidising sewage, there have been periods of activity due to some improvement in the electrolytic plant. This latest period of activity is due to the introduction of the Landreth process, in which lime is added to the sewage, presumably to increase the electric conductivity, and revolving paddles between the electrodes serve to remove the gases which cause polarisation. R. S. Lamphear[14] has reported upon the process as in operation at Easton, Pa., and concludes that the use of the lime without electrolysis produces an equally good result, especially as the amount of lime used at Easton was considered excessive. The subject was discussed by eminent sanitarians at the Cleveland Convention[15] of the American Society for Municipal Improvements, and the Sanitary Engineering Section of the American Public Health Association has appointed a Committee[16] to report upon the process.

A considerable amount of progress in the application of the activated sludge process during the year is to be reported and several new plants are being constructed, but these are for the most part on exactly the same lines as already existing plants.

The experiments of J. D. Watson at Birmingham, to which reference has been made in previous reports, have demonstrated that by a short period of contact between the sewage and activated sludge it is possible to deprive the sewage of its malodorous constituents and at the same time to effect a considerable amount of purification. The sewage thus partially purified can be sprayed over percolating filters without giving rise to nuisance from smell and the rate of filtration can be largely increased. A large unit plant to put these principles into practice is being constructed at the works of the Birmingham Tame and Rea District Drainage Board. The process has been termed "bio-flocculation," and presents some analogy with the older chemical precipitation processes, in some of which the precipitant was capable of regeneration and re-use. If we regard the activated sludge as a biological precipitant, probably the living portion of it plays a double function, firstly in acting like any other non-living material possessed of large surface area as an adsorbent for the organic matter in the sewage, and secondly in being able with the aid of oxygen to regenerate the precipitant or reactivate the sludge The relative magnitude and importance of these two functions is as yet undetermined. If it should be found that the latter function is of the lesser magnitude the advisability of manufacturing activated sludges with inorganic substances as mentioned by

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[14] *Eng. News Rec.*, Aug. 17, 1922, 276.

[15] *Ibid.*, Oct. 19, 1922, 658.

[16] *Chem. Trade J.*, Nov. 17, 1922, 614.

J. H. Garner[17] would be indicated. Such a procedure, by suitable selection of the substrate, might be made to alter entirely the character of the activated sludge and might render it amenable to the ordinary methods of sludge dewatering. Bearing in mind the use of brown coal or lignite in the Rothe-Röckner sewage precipitation process, it might be found that peat or coal dust would form a suitable substrate for the activated sludge, and in such a case the dried sludge with its high nitrogen content could be briquetted,[18] or gasified in producer plant with the production of ammonium sulphate. This would offer an alternative to the production of fertiliser as a commercial outlet for activated sludge, and would afford a means of recovering the nitrogen in sewage in the form of ammonium sulphate. The surface area of such artificial sludges could be increased by the use of the Plauson colloid mill with a possible increase in activity, and the same mill could be used for experiments on the possibility of extracting enzymes from ordinary activated sludges to see whether these would have a coagulating action on the colloidal matters in sewage.

The new tool of research which has been provided by the newer knowledge of the colloidal state of matter collected during the past decade has not yet been intensively applied to the problems of sewage disposal, though there are indications that a re-study of the older chemical precipitation processes in the light of this knowledge would yield valuable results. The Fourth Report[19] on Colloid Chemistry prepared by a Committee of the British Association for the Advancement of Science, and books on "The Chemistry of Colloids and some Technical Applications," by W. W. Taylor[20] and on "Applied Colloid Chemistry," by W. D. Bancroft,[21] serve to indicate the problems and to stimulate to definite lines of research. A paper by N. M. Comber[22] on the characterisation of clay must also be included in this category.

As already stated, most of the new constructional work undertaken during the year in connexion with the activated sludge process has been on the lines of the works which have now been in operation for several years at Manchester and Sheffield, but the experiments which have been carried out by J. Bolton[23] at Bury during the past few years have resulted in the development of an apparatus which is being installed at several works by the

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[17] *Surveyor*, Dec. 15, 1922, 373; Dec. 22, 1922, 393.
[18] E.P. 176,053; *J.*, 1922, 282A.
[19] H.M. Stationery Office.
[20] Longmans, Green & Co.
[21] McGraw Hill Book Co.
[22] *J.*, 1922, 77T.
[23] *Surveyor*, May 26, 1922, 417; June 2, 1922.

Ames-Crosta Engineering Company. In this apparatus the aeration of the mixture of sewage and activated sludge is dependent entirely upon surface aeration. The sludge as it settles to the bottom of the tank is continuously drawn up a central tube and spread over the surface of the liquid in the tank in the form of a film or spray and the incoming sewage mixes with it at this point. Another form of construction for carrying out the activated sludge process has been described[24] during the year. It is termed the "Low-Power" system; the mixing of the sewage and activated sludge in a continuous channel is effected by means of spiral devices placed in the channel, and the return sludge is raised by means of a scoop wheel; aeration is effected at the surface of the liquid by exposure to the atmosphere. The method does not appear to have been adopted or even tried on an experimental scale.

The activated sludge process has now been adopted by a large number of local authorities, and the three largest plants which are under construction at the present time are those at Reading, Sheffield, and Stockport. The first is on the "air-blowing" system and the other two are on the "mechanical agitation" system as worked out by J. Haworth at Sheffield. The experimental plant at Sheffield has dealt successfully during the year with the whole of the flow of sewage from the Tinsley district up to four or five times the dry weather flow of 350,000 gallons per day, but it must be said that the plant is undoubtedly larger than would be designed for such a flow of sewage. The activated sludge plant of the Manchester Corporation at their Withington works has continued to yield excellent results and this Corporation have decided to construct at these works a further unit on the lines of the existing large unit at their Davyhulme works. The Annual Report of the Rivers Department of the Manchester Corporation for the year ending March 29, 1922, was issued towards the end of the year under review. It contains, as usual, a very valuable record of the operations of the Department which is responsible for, amongst other duties, the treatment of the Manchester sewage. The activated sludge unit at the Withington works has dealt with an average daily volume of sewage of 280,000 gallons after a very short preliminary settlement in detritus tanks. The aeration and settlement tanks have capacities of 55,000 and 27,000 gallons respectively. Unfortunately the Report does not give the variations of the flow of sewage, so that it is somewhat difficult to estimate the capacity of the works for dealing with three times the dry weather flow. The total volume of air used for aeration purposes has been equivalent to 1·35 cub. ft. of free air per gallon of sewage treated, and from the average analytical results published in the report it can be said that the effluents have been of a very satisfactory character. The diffusers, which have been in use for over five years, continue to give satisfaction and only indicate a slight increase in friction. The large-scale continuous-flow activated sludge plant at the Davyhulme works has dealt with flows of sewage at rates varying from 240,000 to 2,000,000 gals. per 24 hours, the largest volume treated in any one day being 1,657,000 gals. and the average volume 663,000 gals., with an average air consumption of 1·55 cub. ft. per gallon of sewage treated. With the Davyhulme sewage, containing much trade waste and liable to contain abnormal amounts of oil, the results of the treatment have not been as satisfactory as at Withington, but the purification effected has amounted to 76–81% on the detritus-tree sewage as supplied to the plant and to 80–84% on the crude sewage.

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[24] *Surveyor*, Nov. 10, 1922, 296; *J.*, 1922, 651A.

E. Bartow and G. C. Baker[25] have given a short review of the progress made with the activated sludge process, and E. Ardern[26] has described the plants which have been constructed in the United States of America and Canada, after visiting several of them in the autumn of 1921. In an article on the chemistry of sanitation, A. M. Buswell[27] refers to the purification of sewage. M. F. Diénert[28] has contributed a very able *résumé* to the literature of the activated sludge process.

The cost of installing the activated sludge process will, of course, vary from place to place, according to local circumstances, but information is being gradually accumulated from which it should be possible to give average figures at a later date. Referring to conditions at Sheffield, J. Haworth[29] has stated that on any other lines than activated sludge a scheme for dealing as effectively with the sewage of Sheffield would cost twice as much and occupy six times the area. The only other estimate which has been published is that of H. P. Eddy, G. W. Fuller, and T. C. Hatton,[30] in which the first cost of an activated sludge plant for dealing with the sewage of the North Side Area of the Sanitary District of Chicago, was compared with the first cost of Imhoff tanks, sprinkling filters, and humus tanks. The estimates assume a population of 600,000 in 1920, and 800,000 in 1930, and an average daily sewage flow at that date of 175,000,000 gals., with a maximum flow of

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[25] *J. Ind. Eng. Chem.*, 1922, **14**, 842.

[26] *Surveyor*, Mar. 10, 1922, 217.

[27] *J. Ind. Eng. Chem.*, 1922, **14**, 840.

[28] *Rev. d'Hygiène*, 1922, **44**, 113.

[29] *Surveyor*, Sept. 29, 1922, 198.

[30] *Eng. News Rec.*, Aug. 24, 1922, 324: *Mun. and County Engineering*, Nov., 1922.

263,000,000 gals. Very full details are included, and the following table shows some of these.

COMPARATIVE ESTIMATES OF COST OF NORTH-SIDE SEWAGE WORKS (CHICAGO SANITARY DISTRICT).

(*Based on* 175,000,000 *gals. average and* 263,000,000 *gals. maximum daily sewage flow, or* 220 *and* 230 *gals. per head of population per day.*)

Scheme.	Capital Cost (£).	Annual Cost (£).			
		Capital Charges.	Renewals and Repairs.	Power, Labour, and Supplies.	Total.
Imhoff tanks, etc. ..	3,286,700	221,004	30,596	102,088	353,688
Per million gals. ..	18,780	3·49	0·48	1·60	5·57
Activated sludge, with dewatering and drying ..	2,900,543	196,743	53,291	189,255	439,289
Per million gals. ..	16,574	3·08	0·83	2·96	6·87
Activated sludge, with lagooning ..	2,640,664	179,116	41,090	126,132	346,338
Per million gals. ..	15,089	2·80	0·64	1·98	5·42

In Great Britain the capital cost of the plant has varied from £20,000 to £30,000 per million gals., but these plants have been much smaller than the Chicago plant, for which detailed plans and specifications are now being prepared. The working cost of plants capable of dealing with 1, 2 and 5 million gals. daily dry weather flow of sewage, and up to three times these amounts in wet weather, was given by J. Haworth [31] as £4·22, £3·54, and £3·02, respectively, per million gals. of dry weather flow. These are lower than the American figures, and would be still lower if they were based upon the actual average flow instead of upon the dry weather flow, but they do not include any allowance for loan charges, and are strictly maintenance costs.

The published information on the cost of the activated sludge process is altogether too meagre to permit of any more definite general conclusions than those given above, and they must be regarded more as indications of the order of magnitude than as definite estimates. The power consumption per million gals. has been variously estimated from 15 to 40 h.p., but a strict comparison of the power consumption of the various methods of applying the activated sludge process is still wanting. Again, it is doubtful whether a strict comparison can be based upon the volume of sewage treated, for the strength of the sewage, depending upon the water consumption per head of the population, and upon other factors, should undoubtedly be taken into account, but it is not out of place to enter a very strong plea for a more accurate analysis than it has been customary to make in the past of the cost of the various separate processes which form part of the whole sewage purification process.

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[31] *Surveyor*, Sept. 29, 1922. 198.

The utilisation of sewage sludge as a fertiliser or fertiliser base has not expanded as much as might have been expected, having regard to the substitution of mechanical transport for horse haulage, and the consequent diminution in supplies of stable manure. This is to be attributed to two causes; firstly, to an agricultural depression during the year, and, secondly, to the fact that the railway companies charge higher rates for the carriage of this low-grade fertiliser than for stable manure. Consequently, there has been a tendency to utilise the material only locally where farmers have been in a position to fetch the sludge from the sewage works or the local authority has been able to organise mechanical transport for the purpose. In the neighbourhood of the large towns it has not, therefore, been possible to dispose of the whole of the sludge produced, and in the agricultural districts not nearly as much has been used as would have been had it been available at a price commensurate with its manurial value.

The dewatering of activated sludge to such an extent as to render further drying by heat practicable is still an unsolved problem, which is standing in the way of an increased development of the activated sludge process. The experiments to which reference was made in previous Reports are being continued. As already stated, the experiments have been directed towards altering the character of the sludge after production in order to render it amenable to the ordinary processes of dewatering, and not towards altering the process itself with a view to producing in the first instance a sludge which can be readily dewatered. At Manchester[32] the addition of light mineral matter such as flue dust to the sludge assists pressing and with the Withington sludge, which is very rich in organic matter, this does not materially impair the availability of the plant food constituents, but the amount of flue dust necessary to enable a suitable cake to be produced is so large as to depreciate seriously the value of the cake. Further work is in hand with various other waste mineral matters, and no doubt organic waste materials will also be tried. Experiments on the use of a paper-making machine with acidified sludges have led to the conclusion that in view of the high renewal costs a revolving drum would offer advantage, and the flotation of the sludge by impregnation with gases has not led to a practical result. Without the use of a vacuum it has been found possible to reduce the water content from 98 to 94%, the volume of the sludge being thus reduced by two-thirds, by the use of a rotating wire-mesh cone fed internally or by revolving a gauze cylinder in the sludge itself. From the experience so far gained at Manchester it would appear questionable whether it is practicable to reduce the water content of the sludge below this point, having regard to the possibility of drying such a sludge at low temperatures.

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[32] *Annual Report, Rivers Department,* 1922.

At Houston,[33] Texas, a large plant has been erected by the Maclachlan Reduction Process Co., Inc., for the treatment of activated sludge with sulphur dioxide gas as a preliminary to pressing.

The fertilising value of activated sludge has been investigated by H. D. Brown[34] and the results obtained have been fully reported in the Annual Report for 1920 of the Ontario State Board of Health. The experiments support the conclusions previously arrived at by other investigators.

With regard to the scientific work carried out on the activated sludge process during the year, in addition to that carried out at Manchester by E. Ardern and his colleagues, mention should be made of the work of E. H. Richards and G. C. Sawyer[35] at Rothamsted. These investigators have carried out a careful piece of research directed to a solution of the questions arising with regard to the recovery of nitrogen in the process. They conclude that the ammoniacal nitrogen in the sewage is absorbed, and in being transformed into the body material of the higher organisms such as protozoa, is more readily available as a plant food than the organic nitrogen of proteins. They attribute the high nitrogen content of the sludge to the presence of large numbers of protozoa.

In a paper on the relation between chemical constitution and antiseptic action in the coal-tar dyestuffs, T. H. Fairbrother and A. Renshaw[36] suggested that as a result of their discovery of the selective bactericidal action of the oxazine group of dyestuffs it might be possible to use these dyes for killing protozoa in activated sludge, as these protozoa might be inimical to the process by feeding on useful bacteria. Some laboratory work on the subject has been carried out and a few preliminary experiments on a large scale, but it is not yet by any means certain that the protozoa are as inimical as would appear in the suggestion. It is possible, however, that an abnormal growth of these organisms is the cause of activated sludge at times assuming a very large bulk, and in such cases the addition of dyestuff might be of assistance in overcoming the difficulty encountered in settling a "bulked" sludge.

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[33] *Surveyor*, Sept. 29, 1922, 189; *Eng. News Rec.*, July 27, 1922, 132.

[34] *Eng. News Rec.*, Nov. 23, 1922, 885; *Surveyor*, Dec. 22, 1922, 892.

[35] *J.*, 1922, 62T.

[36] *J.*, 1922, 146R, 134T.

The cost of such a treatment would appear, however, to be prohibitive with the dyestuffs which have, so far, been found suitable.

Experiments in France on the applicability of the activated sludge process to the Paris sewage have been carried out by M. F. Diénert,[37] and L. Cavel[38] has investigated the bacterial purification effected by the process when applied to strong sewage obtained from a system of sewers from which surface water was excluded.

W. E. Adeney[39] (jointly with A. G. G. Leonard and A. Richardson) has made a further contribution to our knowledge of the rate of solution of gases by water and by solutions of sodium chloride, in which he shows that the "streaming" effect is more rapid in salt water than in fresh water, and that the effect reaches to depths of at least ten feet. This "streaming" effect has been described in former papers, and refers to the downward streaming of the surface layers of quiescent liquids exposed to a gas.

Attention may be directed to the Christie Patent Vibratory Process,[40] and the possibility of applying it for the purpose of rendering specially dense sewage sludges pumpable, though such sludges when impregnated with air or other gases, can be made to assume a very liquid form. The process is applied to caustic soda sludge after drying in vacuum filters down to a water content of 45–50%.

The question of sewage disposal in the tropics is receiving increasing attention, and has been the subject of a paper by W. W. Clemesha,[41] before the Royal Sanitary Institute Congress during the year. M. Khalil has shown that in the West Indies septic tanks have no destructive action on the eggs of parasitic worms. His results have been published in the Collected Papers of the London School of Tropical Medicine (Department of Helminthology), No. 16, p. 1.

Liquid Trade Refuse.

During the year under review there has been a trade depression which has to some extent lessened the production of liquid trade refuse, with the result that progress in the construction of works for its treatment has not been very marked.

The most serious class of refuse is that produced at creameries, dairies, and cheese factories. The tendency of the last few years has been for farmers to send their milk to depots where it is pasteurised before being dispatched to the consuming centres, and the excess milk is made into cheese. As a result waste liquids which were formerly produced in small volumes at separate farms, have been concentrated at central depots, and the problem of their disposal has become an acute one for the dairy industry. The waste liquids include whey from the manufacture of cheese, and the washings of churns and utensils used in the various processes, together with floor washings and occasionally a churn of sour milk. It is estimated that at these depots the wastage of milk amounts to 0·5% of the volume received, and as some of these factories receive as much as 8000 or 10,000 gals. per day the volume of milk which finds its way into the liquid wastes may reach 40 or 50 gals. per day. This is diluted with all the washings, but as its oxygen-consuming power is from 100 to 200 times that of ordinary domestic sewage its treatment involves the construction of works of such a size as would deal with 6000 to 8000 gals. of sewage per day. The stream pollution caused by milk depots has been very marked in Somersetshire, and W. G. Savage and D. R. Wood[42] have contributed to our knowledge of the problem and suggested a solution.

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[37] *Rev. d'Hygiène*, 1922, **44**, 113.

[38] *Comptes rend.*, 1922, **174**, 578; *J.*, 1922, 229A.

[39] *Sci. Proc. Royal Dublin Soc.*, 1922, **17**, 19; *J.*, 1922, 781A.

[40] *Chem. Age*, Sept. 23, 1922, 409.

[41] *J. Roy. San. Inst.*, 1922, **43**, 127; *Surveyor*, Aug. 11, 1922, 95.

It is recognised that the whey is of some value on account of its feeding properties, and its utilisation either for pig-feeding or for the manufacture of whey solids or lactose has been advocated by the Ministry of Agriculture and Fisheries. The factory[43] which is now being operated near Crewe for the purpose of demonstrating the possibility of recovering lactose from the whey deals with batches of 1000 gals., and not more than 2000 gals. has been dealt with on any one day, although the factory has a capacity of 3000 gals. per day. Fat and butter are first recovered in a centrifugal machine, and the whey is then heated to 200° F. to separate lactalbumin, which is removed by pressing. The press liquor is neutralised, when further quantities of lactalbumin separate and these are removed by a second pressing. The liquor is then concentrated and allowed to crystallise, yielding crude lactose. The refining of this material will also be undertaken. Up to the present no financial results of the operation of the factory have been published.

Experiments have also been undertaken in this direction by W. D. Whetham[44] at Whitfield, Dorset, at the instance of the Royal Agricultural Society. It is suggested[45] that at small depots the whey should be concentrated to about one-tenth of its original volume and then transported to a factory for the recovery of lactose and lactalbumin.

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[42] *J. State Med.*, July, 1922; *Lancet*, Oct. 7, 1922, 772.

[43] *Chem. Trade J.*, Mar. 10, 1922, 294; *Chem. Age*, Mar. 11, 1922, 312.

[44] *Chem. Age*, Mar. 25, 1922, 370; *Nature*, Mar. 23, 1922, 383; *J.*, 1922, 19R.

[45] *Estates Gazette*, Nov. 18, 1922, 703.

An account of the experiment on the disposal of creamery refuse carried out by A. Poole Wilson[46] for the Department of Agriculture and Technical Instruction for Ireland, to which reference was made in last year's Report, has been published. The creamery sewage, whether containing whey or not, was shown to be amenable to the activated sludge process of purification, and the results were so promising that other experimental plants have been erected, and the process has been brought into operation at one large factory at least.

The application of centrifugal machines for the removal of solid matters from trade refuse has not made much progress, although several experimental plants have been erected.

With regard to the investigations on the treatment of industrial wastes undertaken by the U.S. Public Health Service, a report[47] on the treatment of tomato canning wastes has been published.

Reference has been made in previous reports to the possibility of difficulties arising in the treatment of the refuse from beet sugar manufacture and from flax retting, both of which industries are being re-established in England. The beet sugar factory and the processes of manufacture at the factory of Home Grown Sugar, Ltd., at Kelham, Notts, have been described,[48] but apparently no serious difficulty has yet arisen with regard to the treatment of the effluent. A. J. H. Gauge[49] has described some investigations on the disposal and purification of flax retting effluents, and in his paper are included some analyses of ret waters as well as an account of experiments on the chemical precipitation and biological filtration of these waters.

During the year trouble has been experienced at several gasworks with regard to the disposal of sulphate of ammonia refuse. This has been due to the proposed erection of sulphate plants at small gasworks, and to the unwillingness on the part of local authorities to admit the refuse to their sewers for disposal along with the ordinary sewage of the district. The Royal Commission on Sewage Disposal recommended that, subject to certain safeguards, the refuse[50] should be admitted to the sewers, and found as a result of their investigations that if the volume of the refuse did not exceed 2%[51] of the volume of the sewage it would not seriously interfere with the treatment at the sewage disposal works. T. L. Bailey[52] in his Annual Report on Alkali, etc., Works for 1921 refers to the subject and has devoted a good deal of attention to the matter both in the laboratory and at gasworks. In co-operation with the engineer and manager of the Hornsey Gasworks, he has carried out some large-scale experiments and demonstrated that, by allowing the hot spent liquor to trickle down a scrubber, up which steam and boiler fire gases are passed, the polluting character of the liquor can be reduced by some 50%, so that it should be suitable for admission to the sewers. Presumably the phenoloid substances, to which the polluting character is largely due, are volatilised into the atmosphere.

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[46] *Journal of the Department*, 21, No. 4.

[47] *Bulletin* 118 (Sept., 1921).

[48] *J.*, 1922, 149R.

[49] *J.*, 1922, 177T.

[50] *Third Report*, 1903. *Cd.* 1486. H.M. Stationery Office.

[51] *Ninth Report*, 1915. *Cd.* 7819. H.M. Stationery Office.

[52] H.M. Stationery Office; *Chem. Trade J.*, Aug. 4, 1922, 134.

K. Imhoff[53] has dealt with the treatment of coal-washing refuse, and has suggested the use of a Wolf rotating filter which is similar in construction to the Oliver and Zenith filters. He also suggests the treatment of the refuse by an electro-osmose process, and the briquetting of the coal sludge with sewage sludge from Emscher or Imhoff tanks. The coal sludge when mixed with fine coke can be readily pressed.

G. Hönnicke[54] has described the processes in use at slaughterhouses and at factories in which the bodies of animals are worked up for the recovery of valuable materials. He also deals with the disposal of the wastes from such factories and concludes that although they can be dealt with by biological processes the cost is too great at the present time. He suggests that the liquid refuse, if discharged into a small stream, should be chlorinated to prevent putrefaction until it reaches a larger stream.

E. V. Chambers[55] has dealt with the purification of industrial waste waters with recovery of useful by-products, and described very fully the operations involved in the treatment of waste waters in the woollen and wire-drawing industries. The recovery of hydrochloric acid after use for pickling wire has not hitherto met with much success, but a plant to deal with 1000 gals. per day of such waste pickle has recently been erected at a wire works in the West Riding of Yorkshire. The waste liquor is treated with sulphuric acid and subsequently distilled for the recovery of the hydrochloric acid, and ferrous sulphate is recovered by crystallisation from the residual liquor in the still.

The utilisation of the waste liquids produced in the manufacture of wood pulp has, from time to time, been the subject of inventions, and when it is borne in mind that the amount of wood which finds its way into the waste liquors is equal to that which appears in the finished product there would appear to be much scope for investigation. During the year Lefranc et Cie. have patented a proposal for obtaining butyric and other fatty acids from such waste cellulosic materials. Briefly the cellulose is converted into sugar, which is then fermented by means of suitable bacteria.

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[53] *Gesundheits-Ingenieur*, Oct. 28, 1922, 539.

[54] *Ibid.*, Dec. 2, 1922, 593.

[55] *Proc. Chem. Eng. Group* (*Soc. Chem. Ind.*), Vol. 3.

Among articles dealing with the general question of the treatment of liquid trade refuse those contributed by E. Rolants[56] and A. Beltzer[57] may be mentioned, together with two reports[58] issued by the Industrial Wastes Board of the Department of Health of the State of Connecticut, U.S.A.

River Pollution.

The activity of the past year in the construction of sewage disposal works must have an effect on the condition of the rivers. The General Report[59] of the Thames Conservancy for the year 1921 contains an account of much work being done in the Thames Valley, and the work has been continued during 1922. The special activity has been undoubtedly largely due to the fact that Government grants have been available to assist in carrying out the work, but the pressure of the Local Rivers Authorities and the neglect of works during the previous years have also been factors of importance.

As a result of trade depression there has been a diminution in the volume of trade waste waters discharged to the rivers and Local Authorities have shown a reluctance in compelling manufacturers to construct or extend purification works for dealing with their trade effluents.

The most serious form of pollution which has occurred during the year is that caused by the discharges from milk depots and cheese factories, and this has been specially marked in Somersetshire. The treatment of this kind of refuse has already been described, and there are signs that the evil is being gradually abated.

Some trouble has also been caused by discharges of spent sulphate of ammonia waste from gasworks, more especially in cases where this refuse has been discharged into the sewers of the local Sanitary Authority, but the researches of T. L. Bailey, to which reference has already been made, offer a possible solution of this difficulty. The biological treatment of this class of refuse has been investigated by H. M. Wilson and W. J. Read,[60] and by P. Keim,[61] and its treatment by settlement and aerobic filtration through filters containing iron oxide has been the subject of a patent by the Koppers Co. and R. L. Brown.[62]

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[56] *Chimie et Industrie*, Feb., 1922.
[57] *L'Ind. Chim.*, Mar., 1922, 95.
[58] *Surveyor*, May 19, 1922, 411.
[59] H.M. Stationery Office.
[60] *Report to West Riding of Yorkshire Rivers Board*
[61] *Gesundheits-Ingenieur*, June 3, 1922.
[62] E.P. 161,976; *J.*, 1922, 726A.

River pollution in South Wales has been considered by a Committee[63] which carried out a Regional Town Planning Survey, and they recommended an extension of the policy of constructing trunk outfall sewers to convey the sewage to the sea.

The final report of the Committee, appointed in May, 1919, jointly by the Ministry of Transport and the Ministry of Agriculture and Fisheries, has not yet been issued, but as a result of their investigations the Ministry of Transport,[64] in a Circular issued on April 18, 1922, urged Local Authorities to give a preference to asphaltic bitumen for the treatment of roads, the drainage from which was liable to cause damage to fisheries. J. J. Fox and A. J. H. Gauge[65] have carried out some experiments for the Committee on the determination of tar acids and tar bases in road drainage and muds, and have shown that aqueous extracts of vegetable substances contain phenolic substances. They have shown that by a process of distillation in steam it is possible to separate the substances of vegetable origin from those derived from tar, and thus to distinguish the nature of phenolic compounds found in road washings.

The pollution of streams by the wastes from pulp and paper mills, and from strawboard factories, has received very full consideration in a series of papers by G. C. Whipple,[66] H. W. Clark,[67] and H. B. Hommon.[68]

A symposium on stream pollution and sewage disposal was organised by the American Society of Civil Engineers and the discussion[69] gives a general idea of the position in America. The stream pollution investigations undertaken by the U.S. Public Health Service on the Potomac, Ohio, and Illinois Rivers are models which might well be followed in many cases, and in a memorandum[70] on the future development of these and other investigations S. A. Forbes, E. O. Jordan, and L. Pearse say: "The present status of the stream-pollution problem and its regulation in the United States is somewhat unsettled as regards any established policy throughout the country. There has been, however, a definite trend in the last twenty years towards improving the condition of streams, and, in particular, those streams in which the nuisance is marked. The tendency to-day is also towards the improvement of streams from which water supplies are taken, and further consideration is being given to the conservation of fish life by stream cleaning. The probability is that, as the country becomes more thickly populated, there will be further pressure for better stream conditions, not only from the standpoint of nuisance, but also to relieve the load upon water-treatment plants using such streams as sources of supply. In so far as the stream pollution problem itself is concerned, the status and tendency seem to be fairly clear, with a trend towards the bettering of conditions in the waterways. On the other hand, the status and tendency of regulations are somewhat clouded by the variations in the different States having authority to act within their borders. This is further complicated by the lack of police powers in many States. A general tendency seems to be to give a central body, like the State board of health, sufficient control, in a discretionary way, to advise on sanitary problems in stream pollution. There has not been, as yet, any marked inclination to follow the lead of Ohio in permitting the State to order work constructed under certain stipulated conditions. From the standpoint of regulation of industrial waste pollution, while there is considerable activity, so far this has not always led to a complete solution of the problem, owing to the cost of treatment. The industrial waste problem seems to have been one of more or less local handling, the practice of each State varying considerably. In some States no attempt is made to regulate at all. The indications are, however, that even in States containing the most industries, conditions have come to such a pass that even the industries realise that something must be done. This would seem to favour well-considered action towards regulations.

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[63] *Report to the Ministry of Health*; *Eng. News Rec.*, Nov. 16, 1922, 850.

[64] *Circular* 149 (*Roads*).

[65] *J.*, 1922, 173T.

[66] *Proc. Amer. Soc. Civ. Eng.*, 1922, **48**, 1385.

[67] *Ibid.*, 1922, **48**, 1393.

[68] *Ibid.*, 1922, **48**, 1397.

[69] *Ibid.*, 1922, **48**, 1[illegible].

[70] *U.S. Public Health Reports*, **37**, Aug. 25, 1922, 2049.

"It therefore seems to us that the Public Health Service has, if it desires, a very definite function to perform in the handling of inter-State problems of stream pollution and in the investigation of these, as well as in the investigation of and research into the underlying principles of stream pollution, sewage treatment, water purification, and sanitary science in general. It further seems that there is a very legitimate function in the co-ordination of effort in inter-state relations to a definite policy for all concerned.

"Regulation of the quality of water for inter-state carriers might also properly be reviewed from time to time.

"Our opinion as to the relative prominence of different lines of study is expressed in order of importance as follows: (1) Fundamental studies of basic problems leading to results of general application; for example, studies of analytical methods, the laws of oxygen loss and replacement, the laws covering bacterial death rates, laws governing the efficiency of filtration; the efficiency of methods of waste disposal, and the laws governing the removal of colloids, dehydration of colloids, colour removal from water supplies, etc. (2) Collective studies bringing together scattered observations;

for example, assembling from various sources, material relating to stream pollution conditions, sewage treatment practice, water purification, etc., utilising data available from State and municipal organisations.

"These studies should, if possible, be correlated by enough personal contact, and perhaps laboratory work, to put the methods of reporting and analysis upon a common basis. If practicable, more effort should be made towards standardisation of laboratory methods, and methods of reporting. In this connexion, also, might well be considered the practicability of a semi-annual review of the progress in the fields of sewage treatment, water purification, and sanitary science, with a view to making more easily available in brief compass the special work being carried on throughout the country, as well as summarising progress in the work." This extract from a memorandum prepared jointly by a professor of biology, a professor of hygiene and bacteriology, and a sanitary engineer, who have jointly acted as consultants of the U.S. Public Health Service in matters relating to stream pollution investigations, indicates the trend of events in America. The work already undertaken by the Public Health Service has comprised laboratory studies of the fundamental biochemistry of sewage disposal and water-purification; experimental studies of methods for the treatment of sewage and industrial wastes; fairly extensive studies of sewage disposal by dilution in several typical waterways; surveys of the pollution of coastal waters, with special reference to contamination of shell-fish; and co-operation with States and municipalities in the study of a number of local problems.

Reference has already been made to the co-operation of the officials of the States of New Jersey and Pennsylvania, with regard to the standards to be attained by effluents from the treatment of sewage discharged into the Delaware River, and although the Royal Commission on Sewage Disposal recommended the adoption of standards for effluents in this country no progress has been made towards making such standards legal. The recommendations of the Royal Commission are, however, used as guides in considering the details of any case, and it is therefore very important that the results of tests carried out in various laboratories should be comparable. In this connexion J. H. Garner[71] has shown that in carrying out the test recommended by the Royal Commission for the determination of the amount of dissolved oxygen taken up from aerated water by an effluent in five days it is very important that standard conditions should be observed, and that by using the tap water from different towns different results are obtained.

It will be recollected that the Royal Commission recommended the adoption of different standards, according to the dilution afforded by the river, into which the effluent is to be discharged. The adoption of such a recommendation would involve a good deal of river gauging, and the Department of Scientific and Industrial Research have published a report on current meters for use in river gauging, prepared by M. A. Hogan.[72]

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[71] *Surveyor*, Dec. 15, 1922, 373; Dec. 22, 1922, 393.

Towns' Solid Refuse.

The collection and disposal of towns' solid refuse is being dealt with each year on more systematic and scientific lines.

In England and Wales the amount of towns' refuse is estimated at 10 million tons per annum, and the annual cost of collection and disposal at over £6,000,000.

The problems to be considered in connexion with the collection are the use of mechanical as against horse haulage and the use of covered vehicles. Generally speaking it may be said that mechanical haulage is only less costly when the distances over which the refuse has to be hauled are comparatively long, so that in many towns it is found advisable to adopt both kinds of haulage. The use of covered vehicles to prevent the refuse from being blown about is in all cases very desirable.

Some useful information is to be found in a contribution by F. Wilkinson,[73] on the mechanical equipment of municipal works depots and scavenging and cleansing departments, and a useful review of the methods of collection, disposal, and utilisation of house refuse has been made by J. S. Rae.[74]

With regard to the disposal of this class of refuse, the practice of indiscriminate dumping on tips is diminishing, although it cannot be avoided in all cases, and during the year the Ministry of Health issued suggestions with a view to diminishing the nuisance liable to be caused by such tips. The main precaution to be taken is to cover the refuse tips with soil following deposition.

A Conference[75] of the Metropolitan Boroughs, to which reference was made in last year's Report, has considered the various methods of disposal, which may be classified as :—

(*a*) Dumping on land tips.
(*b*) Dumping in the sea.
(*c*) Burning in destructors.
(*d*) Pulverising by machinery.
(*e*) Screening and grading by machinery.

Only the first two may be regarded as final methods of disposal; destructors yield a clinker which must either be tipped, used for making concrete or roads, or for sewage filters; the other two methods serve to prepare the material for use as a fertiliser or to assist in the salvage of fuel, tins, glass, waste paper, and other constituents. These two methods are coming into increasing use, and works for the salvage and utilisation of towns' refuse are in operation or in course of construction at many places, such as Sheffield, Birmingham, Newark, Eccles, Bo'ness, and Falkirk. The Eccles[76] salvage plant has been described during the year, and J. W. Hipwood[77] has described the methods in use at Newark.

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[72] H.M. Stationery Office.
[73] *J. Inst. Mun. and County Eng.*, 1922, **49**, 89.
[74] *Surveyor*, Sept. 15, 1922, 163.
[75] *J. Inst. Mun. and County Eng.*, 1922, **49**, 486.

Messrs. Ashwell and Nesbit, Ltd., Leicester, have introduced a plant for the production of gas from house refuse, on the lines of producer gas plant. The fuel is furnished by the cinders and vegetable matter in the refuse and the makers have a 50 h.p. plant operating on dustbin refuse.

With regard to general methods of utilisation, the importance of first obtaining an analysis of the refuse cannot be unduly stressed. J. C. Dawes estimates the average analysis to be somewhat as follows: Fine dust, 45%; fuel (cinders of all sizes), 35–40%; vegetable matter, 5–10%; paper and light débris, 4%; metals, 1·0–1·5%; bone, 0·3%; glass, stone, brick, and heavy débris, 12%; and other figures have been published by J. W. Hipwood and others.

The main outlet for the disposal of pulverised or screened refuse is as a fertiliser, especially for use on stiff or heavy land, and Sir E. J. Russell[78] has drawn attention to the value of this material to take the place of stable manure, supplies of which for the large market gardens are rapidly diminishing. Analyses of the material which have been published show that it contains from 1 to 2% of nitrogen, together with variable but small percentages of lime, phosphoric acid, and potash.

Until recently the railway rates for the transport of this material have hindered its proper utilisation, but the railway companies are now prepared to quote special rates, so that the cost of carriage is comparable with that of stable manure.

WATER SUPPLY.

As already stated, the year has been marked by exceptional activity in the construction of works for the supply of water for domestic consumption, due to the fear of another drought such as was experienced in 1921, and to the fact that a Government grant has been available in aid of work undertaken for the relief of unemployment.

It was not until the middle of the year was passed that the danger of a recurrence of the water shortage caused by the 1921 drought could be said to be generally past, and even then in some districts the danger was present. On March 29, 1922, the Ministry of Health issued a circular[79] to Water Authorities, urging them in view of the prevailing shortage to be prepared with measures for conserving or supplementing their supplies and offering to render assistance by furnishing any information in their possession, and so late as June 23, 1922, a further circular[80] was issued drawing attention to the earlier warnings on the matter. Sir A. C. Houston[81] has dealt with the effects of the 1921 drought, more especially with reference to the chlorination of impure water supplies, and C. E. P. Brooks and J. Glasspoole[82] have dealt with the same subject from the statistical point of view.

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[76] *Mun. Eng. and San. Rec.*, Dec. 7, 1922, 627.

[77] *Surveyor*, Aug. 4, 1922, 81.

[78] *J. Ministry of Agriculture*, Nov., 1922; H.M. Stationery Office

The subject of water chlorination has received an increasing amount of attention during the year. In his Sixteenth Annual Report[83] to the London Metropolitan Water Board Sir A. C. Houston gives some interesting information on the continued application of the process to the London water supply derived from the Thames, the New River, and from a deep well, the water from which contained very little oxidisable matter. In the latter case, with a dose of chlorine of 0·25 part per million, no taste could be detected near the works. but occasionally in various parts of the area of supply there arose waves of taste. If this dose was increased or diminished materially, the effect was to impart to the water a chlorinous or an iodoform taste respectively, and it was finally decided to super-chlorinate with a dose of one part per million, and to dechlorinate the water with a solution of sulphur dioxide. After the adoption of this double process all complaints of taste ceased. In some general notes on the future of chlorination Houston summarises the advantages and disadvantages, and undoubtedly shows that the process has a much wider applicability than it has hitherto enjoyed. His description of the methods of administering chlorine to water should prove of inestimable value to all those who propose to adopt the process. In a lecture on "Progress in Water Purification," delivered at the Annual Winter Meeting of the Institution of Water Engineers, Sir A. C. Houston[84] provides much food for thought on the various aspects of the subject from slow sand filtration to chlorination. H. P. Boulnois[85] has contributed a series of articles on the historical aspect of London's water supply.

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[79] *Circular* 288.

[80] *Ibid* 321.

[81] *Hospital and Health Review*, June, 1922, 253.

[82] *Quart. J. Roy. Met. Soc.*, April, 1922.

[83] P. S. King & Son, Ltd.

[84] *Water and Water Engineering*, Dec. 20, 1922, 445; *Surveyor*, Dec. 29, 1922, 407.

[85] *Surveyor*, 1922, May 19, 402; June 2, 434; June 9, 450.

In Canada and the United States of America, especially along the shores of the Great Lakes, questions of water purification are becoming very important if not acute, and much labour has been expended upon scientific investigations of the various problems which arise. Rapid filtration and chlorination have there found more extended application than in this country, and various possibilities have been explored with a view to making use of new ideas. For example, at Toronto where Lake Ontario water has been treated after coagulation with alum in "drifting sand" filters and subsequently chlorinated, N. J. Howard[86] has shown that by the use of chlorine prior to rapid filtration on a plant dealing with 35 to 50 million gallons per day a great saving can be effected, both in the cost of chemicals and in the lessened need for cleaning the rapid filters. The quality of the water of Lake Ontario has deteriorated during the last few years to such an extent that it has been necessary to increase the dose of alum required for coagulation from 1·0 to 2·5 grains per gallon. This had the effect of reducing the output from the filters owing to the more frequent cleansing necessary, and by substituting chlorine for alum at such times as the water was physically good the above-mentioned double saving has been effected. A record of the laboratory work carried out in connexion with the Toronto water supply during 1912 to 1921, has been published by N. J. Howard,[87] the bacteriologist in charge. The publication contains some very satisfactory results of four years' working of the "drifting sand" filter, which was illustrated in the Annual Report[88] for 1919, and records the typhoid death-rates per 100,000 of population, as follows :—

1910*a*	40·8	1914	7·5	1918	3·1
1911	20·0	1915*c*	1·9	1919	2·6
1912*b*	12·1	1916*d*	6·8	1920	2·0
1913	10·4	1917	3·8	1921	3·0

a Raw water chlorinated following epidemic.
b Raw water partly filtered and chlorinated.
c City by-law enforcing pasteurisation of milk became effective.
d Military camp in Toronto, where several cases developed and were scored against city.

Toronto is one of the few places where a scientific control of the water supply is exercised at all comparable with that undertaken by the London Metropolitan Water Board, and it is to be regretted that owing to a limited staff it has been found necessary to limit the work.

The use of alum and chlorine together for the treatment of soft coloured waters has also been discussed by A. L. Gammage[89] as a means of preventing corrosion. Both these chemicals will undoubtedly have an influence upon the hydrogen-ion concentration of the water, and as this is an important factor in corrosion it may be possible to adjust the relative amounts in such a way as to reduce corrosion to a minimum. The question of the residual alum after coagulation also has a bearing on the same point, and a considerable amount of work has been done by W. Gore,[90] W. D. Hatfield,[91] J. R. Baylis,[92] R. E. Greenfield and A. M. Buswell,[93] A. M Buswell and G. P. Edwards,[94] F. Hannan,[95] and others on the influence of the p_H value of the water on this factor. It appears that if $p_H = 6$ a minimum of residual alum is obtained after coagulation. The importance and practical bearing of these investigations upon precipitation and water softening phenomena is only just being realised and therefore reference should be made to some of the pioneer literature on the subject.[96]

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[86] *J. Amer. Waterworks Assoc.*, July, 1922, 606 ; *J.*, 1922, 994A.

[87] *Canadian Eng.*, 1922, **42**, 468 ; *J.*, 1922, 994A.

[88] *Ann. Repts.*, 1919, **4**, 481.

[89] *Eng. News Rec.*, Sept. 7, 1922, 391.

The effect of water supply on vital statistics has received some attention during the year and the use of semi-logarithmic paper in plotting death rates has been advocated by G. C. Whipple and A. D. Hamblen[97] as giving a more marked indication of changes in the curves than ordinary squared paper. For example, by this method it is possible to show accelerations in the gradual decline due to sanitation in the typhoid death-rate in America due to the general introduction of water filtration about 1890, and to milk control and chlorination of water supply between 1908 and 1910.

Two notable cases of epidemics caused by impure water have been reported upon during the year. W. V. Shaw[98] reported to the Ministry of Health upon an epidemic of enteric fever at Bolton-upon-Dearne, and T. W. Wade[99] reported to the Welsh Board of Health on the occurrence of bacillary dysentery in the Ogmore and Garw Urban District in the County of Glamorgan.

L. Pearse and S. L. Tolman, in a paper presented at the Annual Meeting of the American Public Health Association in October, 1922, summarised the position with regard to the water supply of the larger cities around the Great Lakes, and gave statistics on the typhoid fever death rates for those cities and all cities in the United States having populations of 100,000 or over.

[90] *Mun. Eng. and San. Rec.*, July 20, 1922, 61, 62.

[91] *J. Ind. Eng. Chem.*, 1922, **14**, 1038.

[92] *Eng. News Rec.*, Aug. 31, 1922, 351.

[93] *J. Amer. Chem. Soc.*, 1922, **44**, 1435; *J.*, 1922, 682A.

[94] *Chem. and Met. Eng.*, 1922, **26**, 826; *J.*, 1922, 480A.

[95] *Water and Water Engineering*, Mar. 20, 1922, 85.

[96] *U.S. Public Health Reports*, **37**, Feb. 17, 1922, 341; *Water and Water Engineering*, April 20, 1922, 131; Mar. 20, 1922, 85; *Z. Unters. Nahr. Genussm.*, 1921, **42**, 175.

[97] *U.S. Public Health Reports*, **37**, Aug. 18, 1922; *Eng. News Rec.*, Nov. 9, 1922, 776.

[98] *Reports on Public Health and Medical Subjects No.* 12. H.M. Stationery Office.

[99] *Ibid., No.* 14. H.M. Stationery Office.

Perhaps the most serious disadvantage in the use of chlorine for the sterilisation of water is the danger of producing an unpleasant taste, a "chlorinous" taste with large doses and an "iodoform" taste with small doses, with an intermediate dose which does not produce any taste. The bold course, though the more expensive, in such cases is to superchlorinate and then dechlorinate the water with sulphurous acid gas, or the use of permanganate after chlorination is effective in removing the "iodoform" taste. Until the origin of the taste is known it is difficult to suggest other remedies, but some work has been done in this direction during the year by E. Bartow and R. M. Warren,[100] and by N. J. Howard,[101] who has recorded his experience in a paper on "Modern practice in the removal of taste and odour." It is very important that the dose of chlorine should be properly regulated, and this has been done at Toronto by making up several colour standards, which can be matched by the blue colour produced in the sterilised water with starch and iodide. The greatest difficulty is experienced in dealing with the so-called "iodoform" taste, which is attributed to the production of chlorophenols. It has been suggested that the phenolic substances may be derived from vegetable matters present in the water, but the matter requires further investigation.

Besides tastes caused by chlorination Howard deals with those caused by the presence of iron and algal growths, and he points out the possibility of minimal quantities of industrial wastes being the cause of complaints. It would be interesting to observe the effect of chlorination on a water having an algal taste to see whether an excessive "iodoform" taste could be produced. Such odour-producing algæ can be eradicated by the use of copper sulphate, and K. F. Kellerman[102] of the Bureau of Plant Industry, U.S. Department of Agriculture, has given the quantities of this material required to kill various forms of odour-producing organisms, together with the safe limiting amounts which can be used without killing various kinds of fish. Unfortunately, the paper does not state whether the figures refer to the crystallised or the anhydrous copper sulphate.

The use of rapid filters has been the subject of experiments during the year by Sir A. C. Houston,[103] who has considered various possibilities of utilising them with economical advantage, more especially in conjunction with semi-rapid filters. If the rapid filters can be worked at a rate of 200 gals. per sq. ft. per hr., and the semi-rapid filters at a rate of 10 gals. per sq. ft. per hr., the process would seem to offer attractive economic possibilities, when it is borne in mind that the rate of filtration practised by the Metropolitan Water Board is under rather than over 2 gals. per sq. ft. per hour. Subsequent chlorination would undoubtedly render the position safe bacteriologically, but such a water might possibly encourage a variety of growths in the distribution mains. The use of rapid filters for the removal of iron in German waters has been described by K. Kisskalt.[104]

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[100] *Eng. News Rec.*, Nov. 23, 1922, 878.

[101] *J. Amer. Waterworks Assoc.*, 1922, **9**, 766; *Surveyor*, Nov. 3, 1922, 275; *J.*, 1922, 994A; *American City*, Oct., 1922, 306.

[102] *Surveyor*, July 21, 1922; Oct. 27, 1922, 261; Nov. 3, 1922, 270.

[103] *Sixteenth Annual Report*, 23; P. S. King & Son, Ltd.

A very promising development of rapid filtration has been described by H. W. Clark,[105] as a result of experiments carried out for the Massachusetts State Department of Health. He proposes the addition of aluminium sulphate to the sand and the precipitation of hydroxide *in situ* by means of caustic soda. In his experimental filters he used sands having effective sizes varying from 0·25 to 0·11 mm. and of a depth of 4·5 ft. The use of aluminium sulphate works out at 0·2 grain per gallon of water filtered, and rates of filtration of 2·5 to 5·0 million gallons per acre per day can be attained. The filter is washed and the aluminium hydroxide regenerated every two or three months by the use of caustic soda (say 0·5 grain per gallon of water filtered). The cost of filtration, including regeneration, is estimated at 2·78 to 3·05 dollars per million gals., as against 6 to 7 dollars for the ordinary mechanical filtration. The process is to be tested on a large scale at several American water treatment plants.

The loading or dosing of American filter plants has been considered by H. W. Streeter,[106] who gives the U.S. Treasury Department requirements as not more than 500 *B. coli* per 100 c.c. for the raw water, and not more than 2 *B. coli* per 100 c.c. for the effluent from the purification plant. For efficient plants he works out a mathematical relationship for the bacterial content of the raw water, and the effluent as follows: $E = c R^n$, in which E and R represent the bacterial content of the effluent and raw water, respectively, and c and n are constants, as given in the following table :—

	c	n
For gelatin count	4·41	0·27
For agar count	0·23	0·55
For *B. coli* count	0 29	0·30

Too little attention appears to have been devoted to the suitability of the sand used for filtration purposes, especially in Great Britain, and more use should be made of determinations of the " effective size " and " uniformity coefficient " of the sand used.

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[104] *Gesundheits-Ingenieur*, Oct. 14, 1922, 522; *Gas- und Wasserfach*, 1922, 6, 85.

[105] *Eng. News Rec.*, Sept. 28, 1922, 514 ; Nov. 23, 1922, 900.

[106] *U.S. Public Health Reports*, **37**, Mar. 31, 1922, 741.

The filtration and sterilisation of water for use and re-use in swimming 'baths'[107] is receiving increasing attention, and G. M. Fair[108] has drawn attention to the possible use in this connexion of chlorine, copper sulphate, ozone, and ultra-violet rays.

G. J. Fowler and R. R. Deo[109] have carried out experiments on the purification effected in water by means of activated silt, a process analogous to the activated sludge process for treating sewage.

In a paper on the action of natural waters on lead, J. C. Thresh[110] breaks new ground in taking into account the electrical conductivity and p_H values of the waters, and L. Greenburg[111] has traced the contamination of a water supply to the lead flashings on the roof of the building from which rain water was collected and used fo drinking purposes.

The corrosion of iron and steel, often due to an improper treat ment, or an absence of treatment, of water, is a very serious matter and Sir R. Hadfield, in a paper presented to the Institution o Civil Engineers, estimates the world's output of these metals durin 1860–1920 at 1860 million tons, of which 660 million tons was los by rusting in use For the year 1920 he estimates the loss b rusting at 29 million tons, and the cost of this wastage, after allowin for cost of protection, at £700,000,000. The question of corrosio is being thoroughly investigated and has been the subject of a pape by J. W. Shipley,[112] who directed attention to cast iron pipes i alkaline soils. The prevention of corrosion in boilers by de-aeratio or de-activation has been dealt with by F. N. Speller[113] an G. Paris,[114] and the use of barium hydroxide has also bee recommended[115] for this purpose.

Water softening is finding increasing application both for indu trial and domestic purposes, and Messrs. J. Crosfield and Son Ltd.[116] have lately introduced a new material for use in softenin filters. The material is termed Doucil, and is believed to $Al_2O_3.Na_2O.5SiO_2$. E. F. Armstrong[117] has described its prepara tion. Solutions of sodium silicate and aluminate are prepared such strengths that when mixed they set to a jelly, which lat dries to a gel containing 50% of water. This material can then used for softening water, as it is capable of exchanging over 5 of its weight for calcium and magnesium contained in the wate and can be regenerated by the use of salt solutions in the same way as permutit is used and regenerated.

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[107] *Mun. Eng. and San. Rec.*, July 27, 1922, 92; Sept. 21, 1922, 326.
[108] *Lancet*, Dec. 3, 1921, 1398.
[109] *J. Indian Inst. Sci.*, 1921, **4**, 149; *J.*, 1922, 432A.
[110] *Analyst*, 1922, **47**, 459, 500; *J.*, 1923, 159A.
[111] *U.S. Public Health Reports*, **37**, July 28, 1922, 1825.
[112] *J.*; 1922, 311T.
[113] *Water and Water Engineering*, Oct. 20, 1922, 356.
[114] *The Engineer*, Dec. 23, 1921, 677.
[115] *Water and Water Engineering*, Mar. 20, 1922.
[116] E.P. 142,974 and 177,746; *J.*, 1920, 525A; 1922, 372A.
[117] *J.*, 1922, 502R.

The radioactivity of miscellaneous waters has been examined in the U.S. Bureau of Chemistry by W. W. Skinner and J. W. Sale,[118] but the possible effects of this property have not yet been fully investigated.

No legislation has followed the Final Report of the Water Power Resources Committee appointed by the Board of Trade in June, 1918, but the Minister of Health has appointed an Interdepartmental Committee to correlate the various interests of the Government Departments in matters relating to water. P. Griffith[119] contributed a paper on the Conservation and Allocation of National Water Resources to the Annual Congress of the Royal Sanitary Institute, and the British Waterworks Association (Incorporated) and the Institution of Water Engineers jointly considered the recommendations of the Water Power Resources Committee. The Minister of Health appointed a small Committee to advise on the technical problems arising in the treatment of water, and has recently appointed a Standing Advisory Committee, consisting of three representatives from each of the above organisations, to confer with the officials of the Ministry on questions relating to water supply.

During the year the General Assembly of Ohio has enacted amendments[120] to the existing law for enforcing correction of stream pollution and improvement of public water supplies, which give power to the State Board of Health to make inquiries and investigations into existing conditions and to order the construction of works for preventing pollution or improving water supplies.

In conclusion, the writer wishes to express his thanks to all engaged upon work in connexion with the subject of this Report, who have so willingly supplied the information without which the Report could not have been compiled.

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[118] *J. Ind. Eng. Chem.*, 1922, **14**, 949.

[119] *Surveyor*, Aug. 11, 1922, 91.

[120] *U.S. Public Health Reports*, **37**, Aug. 11, 1922, 1945.

FINE CHEMICALS, MEDICINAL SUBSTANCES, AND ESSENTIAL OILS.

By HAROLD KING, D.Sc.,

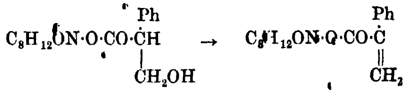
Department of Biochemistry and Pharmacology, The National Institute for Medical Research, Hampstead.

IN the section of applied chemistry covered by the above title the past year has seen steady and solid progress. The one outstanding discovery of the year is the preparation of an extract of the pancreas containing the hormone insulin, and its use for the amelioration of the diabetic condition in man. For a decade or more insulin will be the focus of attention of numerous workers until its great potentialities, both theoretical and practical, are fully explored.

ALKALOIDS.

Hyoscine and Allied Bases.

There are few valuable alkaloids which, from the date of their discovery, have been the subject of more continual controversy than hyoscine. Isolated in 1880 by Ladenburg, and called hyoscine, re-discovered in 1888 by Schmidt, and named scopolamine, and an inactive form named atroscine found by Hesse, two or more decades passed before the discussion as to the identity of these alkaloids subsided. The last decade has been devoted to the difficult and surprising problem of the constitution of hyoscine, and of the basic hydrolytic portion of the molecule, oscine. In the past year the problem was finally settled.[1] It will be recalled that in 1919 the writer showed that hyoscine could be resolved by bromocamphorsulphonic acid,[2] that the active hyoscines when hydrolysed gave optically active tropic acid and optically inactive oscine, and that the hydrolytic product oscine could itself be resolved. This could be interpreted in at least two ways: either a symmetrical oscine occurs in the esterified state in hyoscine, and on hydrolysis gives an unsymmetrical oscine, or *d*- and *l*-hyoscines were partially racemic esters owing their activity to the tropyl portion of the molecule and theoretically capable of further resolution. An attempt[3] to decide this point in favour of the second hypothesis by conversion of *l*-hyoscine into inactive *apo*hyoscine



$$C_8H_{12}ON{\cdot}O{\cdot}CO{\cdot}\overset{Ph}{\underset{CH_2OH}{CH}} \rightarrow C_8H_{12}ON{\cdot}O{\cdot}CO{\cdot}\overset{Ph}{\underset{CH_2}{\overset{\|}{C}}}$$

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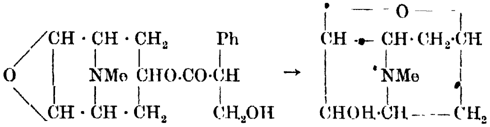
[1] K. Hess and O. Wahl, *Ber.*, 1922, **55**, 1979; *J.*, 1922, 683A.

[2] H. King, *Chem. Soc. Trans.*, 1919, **115**, 476.

[3] H. King, *Chem. Soc. Trans.*, 1919, **115**, 974.

and resolution of *apo*hyoscine was not successful in the latter respect. Hess and Wahl have, however, now gone a step further and have reduced the double bond in *apo*hyoscine with production of hydratropyloscine. They find that it is not identical with either of the two racemic esters formed by esterification of oscine with hydratropic acid. This can only mean that oscine in hyoscine exists in a perfectly symmetrical state, but becomes unsymmetrical on hydrolysis.



When the bases of coca leaves are hydrolysed a number of acids are found whose esters have never been isolated from the crude alkaloidal bases. The basic hydrolytic products may, of course, be identical with known bases such as ecgonine or *pseudo*tropine, but that this is not entirely so is shown by the recent isolation[4] of a new crystalline base, $C_8H_{15}ON$, isomeric with tropine and *pseudo*tropine, from the basic residues after removal of ecgonine. It has been characterised by preparation of salts, and of its benzoyl derivative and methiodide. It would be interesting to know whether it is optically active, and to what degree its benzoyl, mandelyl, and tropyl esters are pharmacologically active.

In this connexion an account of an attractive piece of work has been published by J. v. Braun and his co-workers.[5] The benzoyl and tropyl esters of a series of β- and γ-hydroxyalkylamines of the types

$NR_2{\cdot}CH_2{\cdot}CH_2OH$	$NR_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH$
$R:N{\cdot}CH_2{\cdot}CH_2OH$	$R:N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2OH$
β-type.	γ-type.

have been prepared. The benzoyl derivatives of the γ-type are more active physiologically than those of the β-type, whereas the reverse holds for the tropyl derivatives. In the secondary bases, where R : N – is the piperidine or pyrrolidine group, the six-membered ring confers the greater physiological activity, both on the mydriatic and cardiac action of the tropyl derivatives and the anæsthetic action of the benzoyl derivatives. These observations amplify some earlier findings[6] of the same worker and his assistants, when they showed that in a series of compounds,

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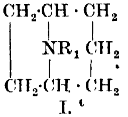
[4] J. Tröger and K. Schwarzenberg, *Arch. Pharm.*, 1921, **259**, 207; *J.*, 1922, 116A.

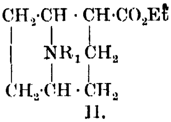
[5] J. v. Braun, O. Braunsdorf, and K. Räth, *Ber.*, 1922, **55**, 1666; *J.*, 1922, 608A.

[6] J. v. Braun, K. Räth, *Ber.*, 1920, **53**, 601; *J. Chem. Soc.*, 1920, i., 446; v. Braun and E. Müller, *Ber.*, 1918, **51**, 235; *J.*, 1918, 281A.

$R:NR_1$ where $R_1=(CH_2)_nOH$, and where $R:N$ was the nortropane ring (I.), the esterified norhydroecgonidine ring (II.), or the corresponding anhydro-derivatives, the maximum anæsthetic action of the benzoyl compounds was observed when n=3, and the maximum cardiac and mydriatic action of the tropyl compounds when n=2.

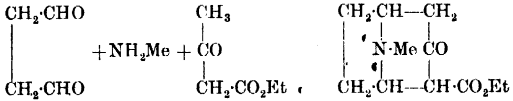


I.



II.

The happy idea of R. Robinson and A. Lapworth of the possibility of a synthesis of tropinone from succindialdehyde, methylamine, and acetone, or a derivative, was carried into effect[7] by Robinson in 1917. The past year has seen the exploitation of this reaction, and the filing of patents in various countries by foreign workers. Tropinonedicarboxylic acid esters[8] are obtained when acetonedicarboxylic acid or derivatives are used, and careful hydrolysi leads to the production of tropinonemonocarboxylic acid esters These may, however, be obtained directly by condensation o succindialdehyde, methylamine, and acetoacetic ester.[9]



If the condensation of succindialdehyde, methylamine, an acetonedicarboxylic acid be effected in the presence of 3% sodium amalgam in weakly acid solution a mixture of amino-alcohols i formed by reduction of the keto-group, and from this a methy ester identical with methylecgonine is obtained.[10] On benzoylatio this gives *r*-cocaine. *r*-Cocaine has never been resolved into it two enantiomorphs, and it would be of great interest to hav recorded the pharmacological properties of the missing *d*-cocaine It would be too much to hope that it possessed the valuable proper ties of *l*-cocaine without its undesirable ones.

Cinchona Alkaloids.

The great value of the cinchona group of alkaloids to humanit may be gauged by the fact that eight million pounds of factor bark, that is to say, bark of high quinine content and low conten of other alkaloids, is consumed annually in the British Empir alone. Of this quantity seven million pounds is supplied from sources outside the Empire, chiefly Java.[11] The proved efficacy of the cinchona alkaloids, both prophylactically and as a cure in malaria, and in a minor degree for the alleviation of the condition of auricular fibrillation and other cardiac irregularities, is ample justification for the enormous attention now being devoted to this group. Fortunately the great output renders these alkaloids fairly readily accessible in quantity, and their known complex constitution and manifold reactivities lend themselves with peculiar ease to experimental work. A reaction which is doubtless of valuable commercial application is the observation of E. Speyer and A. G. Becker, that quinine, hydroquinine, quinidine, hydrocupreine, and ethylhydrocupreine react with 30% hydrogen peroxide to give amine-oxides, the original bases being regenerated by the action of sulphurous acid.[12] This protection of one of the tertiary nitrogen atoms facilitates the preparation of O-alkyl derivatives of hydrocupreine without formation, at least as far as one nitrogen atom is concerned, of quaternary bases during methylation.[13]

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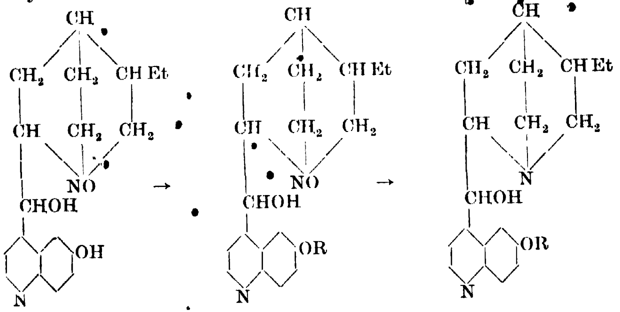
[7] *Chem. Soc. Trans.*, 1917, **111**, 762; *J.*, 1917, 1062.

[8] E. Merck, O. Wolfes, and H. Maeder, G.P. 354,950, *J.*, 1922, 787A; E.P. 164,757, *J.*, 1922, 436A. E. Merck, G.P. 344,031, *J.*, 1922, 270A; E.P. 153,018, *J.*, 1922, 270A.

[9] E. Merck and O. Wolfes, E.P. 153,917; *J.*, 1922, 436A.

[10] E. Merck, O. Wolfes, and H. Maeder, G.P. 354,696; *J.*, 1222, 787A.



The well-known American workers in this group, W. A. Jacobs and M. Heidelberger, have described a large number of interesting derivatives during the past year. As these workers are chiefly concerned with the preparation of these substances for determination of their bactericidal action, mainly on pneumococcus, it would be a welcome change to receive some brief statement of the activity in the chemical portion of their paper. This lacuna was particularly noticeable in the vast number of arsenic compounds described by these authors, only one of which, tryparsamide, as was shown subsequently, proved to have any noteworthy spirochaeticida action. These authors have described[14] diamino-, aminohydroxy-

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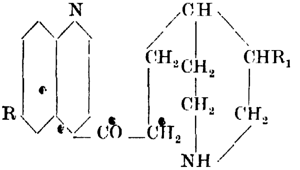
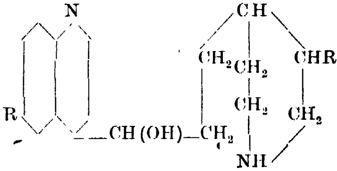
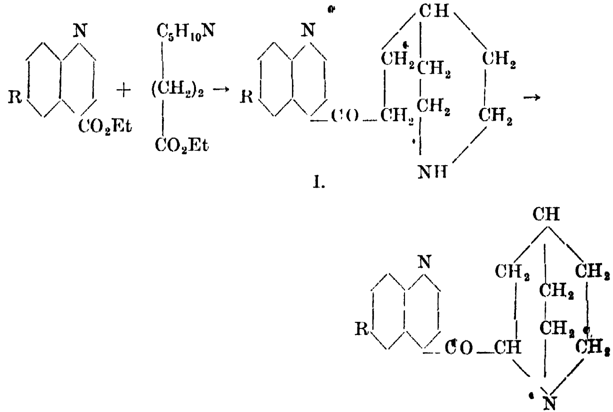
[11] *J.*, 1922, 512R; *Lancet*, 1922, 2, 526.
[12] *Ber.*, 1922, **55**, 1321; *J.*, 1922, 516A.
[13] Vereinigte Chininfabr. Zimmer u. Co., G.P. 344,140; *J.*, 1922, 439A.
[14] *J. Amer. Chem. Soc.*, 1922, **44**, 1073; *J.*, 1922, 516A.

and dihydroxy-derivatives of quinine, substitution taking place in the phenyl nucleus of the quinoline group. Of equal interest are the hydro-derivatives of hydrocinchonine, cinchonine, and hydroquinine, produced by reduction with sodium and amyl alcohol.[15] The quinoline nucleus may take up four hydrogen atoms in the usual way, and in addition the >CHOH group may be reduced with production of deoxy-bases. The isolated observations of a number of workers are thus linked up and elucidated. The toxines produced by the action of dilute acids on the cinchona alkaloids contain a keto group, and this may now be reduced by hydrogen and palladium to an alcoholic group, thus giving rise to the hitherto unknown alcohols.[16] Thus, quinotoxine (quinicine) and cinchotoxine (cinchonicine) give dihydroquinicinol and dihydrocinchonicinol, respectively.





On the synthetic side P. Rabe, K. Kindler, and O. Wagner, in continuation of their valuable series of syntheses in this group, have now synthesised[17] 9-rubatoxanone (I.), 9-rubanone (II.), (R=H) and the corresponding 6¹-methoxy-derivatives (R=OMe).



I.

II.

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[15] W. A. Jacobs and M. Heidelberger, *J. Amer. Chem. Soc.*, 1922, **44**, 1079; *J.*, 1922, 516A.

[16] *J. Amer. Chem. Soc.*, 1922, **44**, 1098; *J.*, 1922, 517A.

[17] *Ber.*, 1922, **55**, 532; *J.*, 1922, 267A.

It will be noticed that I. is, in reality, vinyl-free cinchotoxine (R=H) or quinotoxine (R=OMe), and II. is vinyl-free cinchoninone or quininone, and on reduction of the CO group, II. should yield vinyl-free cinchona alkaloids containing two asymmetric carbon atoms instead of the usual four.

Quinidine is rapidly establishing for itself a place in modern cardiac therapy. From a variety of sources[18] there are records of the restoration to normal rhythm in about 50% of the cases of auricular fibrillation treated. T. Lewis and his co-workers[19] find that quinidine is five to ten times as powerful as quinine, but that hydroquinidine, the chief impurity in commercial quinidine, is slightly more active than quinidine itself.

SIMPLE NATURAL BASES AND ANIMAL PRODUCTS.

Of only one of the secretions of the ductless glands constituting the hormonopoetic system, namely adrenaline, can the chemistry be said to be satisfactory. Adrenaline has been synthesised and the synthetic product is a commercial article and is used extensively as a hæmostatic and in asthma. Other bases of comparable activity are known, and attempts have been made in Germany to popularise 3.4-dihydroxyphenylethanolamine, $(HO)_2C_6H_3CHOH.CH_2.NH_2$. Thyroxin, the hormone of the thyroid gland, has been obtained crystalline by Kendall, but there is some doubt in the minds of chemists as to its exact formula, and synthetic substitutes are completely lacking. The hormone of the infundibular portion of the pituitary gland has not yet been isolated pure. This is chiefly due to its labile nature and the difficulty of accumulating it in quantity. J. J. Abel and C. A. Rouiller have recently claimed[20] that a clean-cut separation of the non-specific depressor substances from the pressor-oxytocic substances can be effected by precipitation of the crude extract with mercuric chloride, the depressor substances being left in solution. The specific oxytocic substance deteriorates on keeping, but the authors claim to have been able to reprecipitate it without loss of activity, the product then being 55 times as active on the guinea-pig's uterus (oxytocic activity) as histamine. On this basis the posterior lobe of the hypophysis of the ox would contain only two milligrams of the hormone. Contrary to Dudley's findings,[21] the authors adduce evidence that the specific vasomotor, oxytocic, and renal actions are but the expression of the manifold physiological properties of one and the same hormone.

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[18] C. C. Wolferth, *Amer. J. Med. Sci.*, 1921, **162**, 812; W. W. Hamburger and W. S. Priest, *J. Amer. Med. Assoc.*, 1922, **78**, 187; F. M. Smith, *ibid.*, 1922, **78**, 877; P. D. White, *ibid.*, **79**, 782.

[19] T. Lewis, A. N. Drury, A. M. Wedd, C. C. Iliescu, *Heart*, 1922, **9**, 207.

[20] *J. Pharm. Exp. Ther.*, 1922, **20**, 65.

[21] *Ann. Repts.*, 1921, **6**, 523.

Of insulin, the hormone of the pancreas, we know practically nothing chemically. Its existence has long been postulated, but it has been the happy lot of two young Canadian workers, F. G. Banting and C. H. Best, to prepare extracts of the pancreas which have the property of lowering the sugar content of the blood of normal and diabetic individuals.[22] It is supposed that insulin is an internal secretion of the islets of Langerhans (ductless glands) of the pancreas, and that it passes directly into the blood or the lymph, whereas the other cells of the pancreas excrete pancreatic juice into ducts. By fractional precipitation of an extract of minced pancreas with alcohol, J. B. Collip, in collaboration with these workers, has succeeded in making an active preparation which is insoluble in alcohol, contains little salts, a trace of protein, and no lipoid.[23] When given in regulated doses twice daily to diabetic individuals, it alleviates the symptoms of diabetes and restores the patients to more normal conditions.[24] It is, however, too early to state whether a cure can be effected through a stimulation to reactivity of the impaired function of the islets of Langerhans. In due course, insulin will doubtless be crystallised, identified, and synthesised. Possibly improvements will be made upon it which will obviate the present complications of hypodermic injections twice daily. As to its mode of action little is known; it is possibly a co-enzyme to the liver enzymes concerned in the storage of glycogen. An excellent review of the recent developments has been given by J. J. R. Macleod.[25]

The past year has witnessed unexpected developments in the chemistry of toad venom. H. Wieland and R. Alles have found[26] that bufotalin is not the real poisonous principle of the common toad, but a nitrogenous substance, bufotoxin, $C_{40}H_{62}O_{11}N_4$, which on hydrolysis gives bufotalin, $C_{26}H_{36}O_6$, which is the acetyl derivative of bufotalein, and suberylarginine, $C_{14}H_{26}O_5N_4$. The latter on hydrolysis gives suberic acid and the amino-acid arginine. In this connexion it is of interest that Faust many years ago isolated two crystalline nitrogenous poisons, samandarine and samandaridine, from the skin of the newt.[27]

A new aspect of the problem presented by muscarine, the very dangerous toxic constituent of the common Fly Agaric, has been revealed by some experiments of the writer.[28] It had previously been thought from the early work of Harnack that muscarine was the aldehyde, $N(CH_3)_3Cl.CH_2.CH(OH)_2$, corresponding to the alcohol choline, but the synthetic experiments of Fischer, Berlinerblau, and others completely failed to confirm this. The writer finds no valid evidence for a relationship with choline; rather is muscarine a more complex base with a molecular weight above 200. The quantity of muscarine in the fresh fungus is very small, 0·4 gram in 25 kg., and this coupled with its other properties renders its isolation difficult. The chief interest of muscarine lies in its extreme specificity of localisation in the mammalian body, and its complete antagonism by atropine.

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[22] *J. Laborat. Clin. Med.*, 1922, **7**, 251; *Amer. Chem. Abst.*, 1922, **16**, 1980.

[23] J. J. R. Macleod, F. G. Banting, C. H. Best, J. B. Collip, J. Hepburn, E. C. Noble, *Amer. Chem. Abst.*, 1922, **16**, 3115.

[24] F. G. Banting, C. H. Best, J. B. Collip, W. R. Campbell, A. A. Fletcher, *ibid.*, 1616.

[25] *Brit. Med. J.*, 1922, **2**, 833; *cf. J.*, 1922, 537R.

[26] *Ber.*, 1922, **55**, 1789; *J.*, 1922, 607A.

[27] *Arch. exp. Path. Pharm.*, 1898, **41**, 229; 1899, **43**, 84.

[28] H. King, *Chem. Soc. Trans.*, 1922, **121**, 1743; *J.*, 1922, 875A.

GLUCOSIDES AND NEUTRAL PRINCIPLES.

In the important but extremely difficult group of digitalis there is little to report, but a sure stepping stone to the chemistry of this group is to be found in certain more readily accessible and related heart poisons. Jacobs and Heidelberger have lately published the first of a series of communications on strophanthin.[29] Strophanthidin, the genin produced by hydrolysis, contrary to the work of Windaus and Hermanns, appears to have the formula $C_{23}H_{32}O_6$. It possesses a double bond, a lactone group, and an alcoholic hydroxyl group. Digitonin, the chief inert glucoside of digitalis, is being investigated by A. Windaus and K. Weil, who find that on hydrolysis it gives digitogenin—containing three hydroxyl groups—a hexose, and a pentose.[30]

$$C_{55}H_{90}O_{29} + 5H_2O \rightarrow C_{26}H_{42}O_5 + 4C_6H_{12}O_6 + C_5H_{10}O_5$$

Closely allied to the above substances is scillaren, the toxic principle of the squill (*Scilla maritima*), which has been isolated by A. Stoll, and is now on the market.[31] No description of its chemical properties or of its method of isolation has, so far as the writer has been able to find, yet appeared. To this group also belong the saponins. A. W. van der Haar finds that hederagenin, the genin from hederin, the saponin of the ivy, and other sapogenins are closely related to the terpene hydrocarbons on the one hand, and to phytosterol-like substances on the other.[32] There is a distinct trend of opinion, based on a variety of evidence, towards the view that this group of heart poisons from animal and vegetable sources is related to phytosterol, cholesterol, and the polyterpenes. The time does not seem premature for synthetic experiments on glucosides prepared from some of these genins or hydroxylactones and various hexoses and pentoses with a view to their application in cardiac therapy.

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[29] *J. Biol. Chem.*, 1922, **44**, 253.

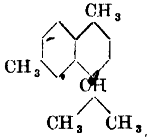
[30] *Z. physiol. Chem.*, 1922, **121**, 62; *J.*, 1922, 684A.

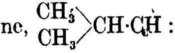
[31] *Compare* W. Straub, *Deut. Med. Woch.*, 1922, **24**, 793.

[32] *Rec. trav. chim.*, 1921, **40**, 542; *J. Chem. Soc.*, 1921, i., 877; *Ber.*, 1921, **54**, 3142; *J. Chem. Soc.*, 1922, i., 160.

ESSENTIAL OILS.

The past year has witnessed an important step forward in the unravelling of the difficulties attending the investigation of the sesquiterpene group. This group lies between the valuable odoriferous terpenes, whose constitution and inter-relationships have been worked out in detail, and the polyterpenes, whose highest member is rubber, and whose lower members are related to cholesterol, the phytosterols, the bile acids, resin acids, genins and a great variety of important natural products. L. Ruzicka and J. Meyer showed in 1921 that the sesquiterpene, cadinene, $C_{15}H_{24}$, from oil of cade and oil of *Juniperus oxycedrus*, is converted by heating with sulphur into cadalene, $C_{15}H_{18}$, with loss of six hydrogen atoms.[33] The former author with C. F. Seidel has now synthesised cadalene which proves to be 1.6-dimethyl-4-isopropylnaphthalene.[34]



(an important adjunct in arriving at possible constitutions fo sesquiterpenes or derivatives is the hypothesis of their formation by polymerisation of isoprene,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH{\cdot}CH:CH_2$, the branched chain of which limits the possible formulæ). The same mode of dehydrogenation, namely, heating with sulphur, facilitates the division of a number of sesquiterpenes into two groups depending on whether they give cadalene or eudalene.[35] The constitution of the latter $C_{14}H_{16}$, is not known, but during its formation by dehydrogenation a methyl group is lost. Like cadalene, it is a naphthalene hydrocarbon. To the cadalene class belong calamenenol and its degradation product calamene, and calamenene, all from oil of calamus *iso*zingiberene and zingiberene from oil of ginger, and the sesquiterpene alcohol, $C_{15}H_{26}O$, from Javanese citronella oil, whilst to the eudalene class belong selinene, from oil of celery, and eudesmol and eudesmene from eucalyptus oil. The formation of these naphthalene hydrocarbons does not prove the existence of the naphthalene nucleus preformed in the sesquiterpenes, but indicates, rather the possession of a potential bicyclic structure. Thus, monocyclic zingiberene yields cadalene.

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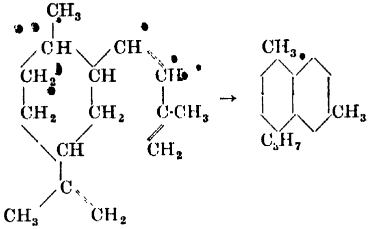
[33] *Helv. Chim. Acta*, 1921, **4**, 505.

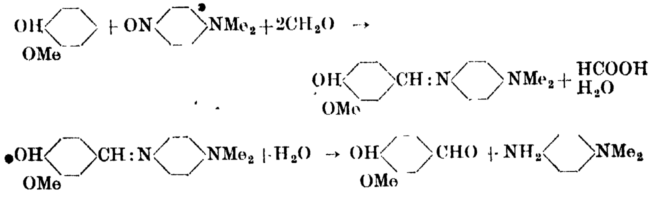
[34] *Ibid.*, 1922, **5**, 369 ; *J.*, 1922, 483A.

[35] L. Ruzicka, J. Meyer, and M. Mingazzini, *Helv. Chim. Acta*, **1922**, **5** 345 ; *J.*, 1922, 482A.



Santonin, $C_{15}H_{18}O_3$, an important vermifuge shows an interesting relationship to this group in that it is a derivative of 1.4-dimethyl-6-isopropylnaphthalene, an isomeride of cadalene.

Hydroxyaldehydes of the aromatic series or their esters are substances of fundamental importance in perfumery and its allied branches. For the preparation of vanillin, which finds extensive use in confectionery, a novel reaction has been patented in various aspects.[36] By heating together a phenol or a phenol ether, such as phenol, anisole, or salicylic acid, with formaldehyde and an aromatic nitroso-compound, such as nitrosobenzene, nitrosophenol, nitrosodimethylaniline, or nitrosodiethylaniline in methyl or ethyl alcohol or even in the absence of a solvent, and saturating continuously with hydrogen chloride, an aldehyde is formed from the phenol and an amine from the nitroso compound. The stages of the reaction may be represented thus in the case of vanillin.



The usual mode of preparation of vanillin is from an ester of *iso*eugenol by oxidation with ozone or bichromate. A recent Swiss patent carries out the operation with bichromate in presence of *p*-aminobenzoic acid in 50% sulphuric acid.[37] The choice of the most suitable oxidising agent is dependent on a variety of conditions, of which the yield is not least important. A study of the oxidation of *iso*safrole to piperonal (heliotropin) $CH_2O_2 : C_6H_3.CHO$, the basis of cheap soap perfumes, has been made by S. Nagai.[38] By oxidation with bichromate and sulphuric acid a 47% yield was obtained, but with potassium permanganate only 8%. Ozonised air, containing 2 to 3·5% of ozone, however, when passed into a solution of *iso*safrole in dry carbon tetrachloride or other inert solvent, gave an ozonide which, on stirring with 35% sodium bisulphite solution, gave an 85% yield of the bisulphite addition product of piperonal.

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[36] Soc. Chim. des Usines du Rhône, E.P. 161,679 ; *J.*, 1921, 448A ; E.P. 164,715 ; *J.*, 1922, 197A ; E.P. 160,765; *J.*, 1922, 566A.

[37] W. C. Sievers and L. Givaudan & Co., Swiss Pat. 89,053 ; *J. Chem. Soc.*, 1922, i., 38.

Coumarin finds an extensive use in perfumery, and as an addition to snuff. A methylcoumarin can be prepared from *m*-cresol and malic acid in 50% yield by condensation in presence of sulphuric acid.[39] The perfume value of methylcoumarin is claimed to be equal to that of coumarin, but its taste is slightly less intense than that of the natural product. This might be a suitable method of utilising malic acid, which is a by-product in the manufacture of maple sugar.

ANÆSTHETICS AND HYPNOTICS.

Anæsthetics.—From time to time there occurs in the literature of anæsthesia the statement that pure ether is unsuitable for anæsthesia or, in a more definite form, pure ether is not an anæsthetic. Within the last few years, two observers, J. H. Cotton in Canada,[40] and Mackenzie Wallis in this country,[41] have definitely stated that pure ether is not an anæsthetic. A perusal, however, of their papers shows that the evidence adduced in support of their claim is very slight. Cotton ascribed the anæsthetic action to dissolved carbon dioxide or ethylene, and as a result of his experiments put on the market an ether containing ethylene 2% by volume, carbon dioxide ½% by volume, and ethyl alcohol 1% by weight. Wallis, in a more lengthy communication, ascribes the anæsthetic properties to ketones, "middle members of the series," and accordingly introduced the commercial preparation "ethanesal." R. L. Stehle and W. Bourne have recently[42] examined the anæsthetic properties of ether prepared by the interaction of sodium ethoxide and ethyl iodide. They state that such ether has in the highest degree the anæsthetic properties which are usually attributed to it. The claim by these latter authors that such ether is free from the constituents which have been claimed as the real anæsthetic agents of ordinary ether is probably true as regards ketones and carbon dioxide, but seems doubtful in respect of dissolved ethylene or ethane.

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[38] *J. Chem. Ind. Japan*, 1922, **25**, 631; *J.*, 1922, 835A; *J. Coll. Eng., Tokyo*, 1921, **11**, 83; *J.*, 1921, 903A.

[39] G. C. Bailey and F. Boettner, *J. Ind. Eng. Chem.*, 1921, **12**, 905; *J. Chem. Soc.*, 1921, i., 879.

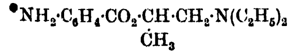
[40] *J. Can. Med. Assoc.*, 1917, **7**, 769.

[41] *Lancet*, 1921, i., 1173.

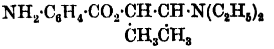
[42] *J. Amer. Med. Assoc.*, 1922, **79**, 375.

Of greater scientific value and interest are some observations on the possibility of the use of pure acetylene as an anæsthetic. Nitrous oxide as a general anæsthetic in combination with oxygen is incapable of producing a deep anæsthesia, owing to the fact that the partial pressure of nitrous oxide necessary for deep anæsthesia cannot be obtained (except under a total increased pressure of the system nitrous oxide plus oxygen), owing to the necessity of keeping up the partial pressure of oxygen. According to H. Wieland, acetylene overcomes this difficulty, the anæsthesia producible by a given partial pressure of acetylene being greater than that by an equal partial pressure of nitrous oxide.[43] Apart from Wieland's experiments on animals and a few on himself, no record of clinical trials appears to have been published. The purification of acetylene for anæsthesia is the subject-matter of a patent by Wieland and Boehringer.[44]

Among local anæsthetics no entirely novel type can be recorded during the past year, the developments being rather along well-known themes. Butyn, $NH_2.C_6H_4.CO_2(CH_2)_3\cdot N(C_4H_9)_2$, is an extension of the novocaine type, and was briefly mentioned last year.[45] Some clinical reports[46] of its use are favourable, but require to be substantiated by long practice. It can replace cocaine, having a quicker action and producing a more profound result with less material; it is stable and does not dilate the pupil. Whether it has the undesirable properties of cocaine is not known. E. Fourneau and J. Puyal have prepared homologues of novocaine and allied bases starting from propylene, butylene, and amylene.[47] These were converted into bromohydrins, which react with dimethyl amine or diethylamine, with production of amino-alcohols which can be benzoylated. The hydrochlorides of *p*-aminobenzoyldiethylaminopropanol (I.), and *p*-aminobenzoyldiethylaminobutanol (II.), have a stronger anæsthetic action than novocaine, whilst the


$NH_2\cdot C_6H_4\cdot CO_2\cdot \underset{CH_3}{CH}\cdot CH_2\cdot N(C_2H_5)_2$

I.


$NH_2\cdot C_6H_4\cdot CO_2\cdot \underset{CH_3}{CH}\cdot \underset{CH_3}{CH}\cdot N(C_2H_5)_2$

II.

hydrochloride of *p*-aminobenzoyldimethylaminodimethylethylcarbinol, $NH_2.C_6H_4CO_2\cdot C(Me)(Et).CH_2.N(CH_3)_2$, has a very intense anæsthetic action. Belonging to the same group are the anæsthetic substances obtained by combination of benzyl alcohol,[48] γ-dibutylaminopropyl,[49] γ-diallylaminopropyl, or β-diallylaminoethyl[50] alcohols with p-nitrobenzoyl chloride and subsequent reduction of the nitro-group.

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[43] *Arch. exp. Path. Pharm.*, 1921, **92**, 96.

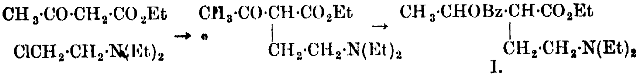
[44] E.P. Appl. 20,241, of 1922; *J.*, 1922, 656A.

[45] *Ann. Repts.*, 1921, **6**, 535.

[46] W. M. Beaumont, *Lancet*, 1922, **2**, 304; *Brit. Med. J.*, 1923, i., 57; *Brit. J. Ophth.*, 1922, 316. A. F. Bulson, *J. Amer. Med. Assoc.*, 1922, **78**, 343, 431.

[47] *Bull. Soc. Chim.*, 1922, **31**, 424; *J.*, 1922, 518A.

Of an aberrant type are the local anæsthetics derived from ethyl acetoacetate or its derivatives[51] by combination of its sodium salt with β-dimethylamino-α-chloroethane or β-diethylamino-α-chloroethane, reduction of the ketonic ester formed and subsequent benzoylation. Ethyl α-diethylaminoethyl-β-benzoxybutyrate (I.) produced in this way is said to possess valuable anæsthetic properties.



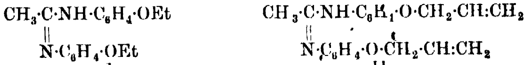
$$\begin{array}{c}\mathrm{CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et} \\ \mathrm{ClCH_2{\cdot}CH_2{\cdot}N(Et)_2}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_3{\cdot}CO{\cdot}CH{\cdot}CO_2Et} \\ \quad\;\;| \\ \quad\mathrm{CH_2{\cdot}CH_2{\cdot}N(Et)_2}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_3{\cdot}CHOBz{\cdot}CH{\cdot}CO_2Et} \\ \qquad\qquad\;\;| \\ \qquad\quad\;\;\mathrm{CH_2{\cdot}CH_2{\cdot}N(Et)_2}\end{array}$$

I.

By combination of ethylene oxide with ethyl p-aminobenzoate (anæsthesin), J. Landrivon and J. Altwegg have prepared mono- and di-substitution derivatives, which are claimed as suitable for use as local anæsthetics in dentistry.[52]

$\mathrm{CH_2OH{\cdot}CH_2{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2Et}$ $\qquad$ $\mathrm{(CH_2OH{\cdot}CH_2)_2N{\cdot}C_6H_4{\cdot}CO_2Et}$

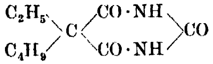
The amidine type of anæsthetic represented by holocaine (I.) is, as is well known, produced by condensation of phenetidine and phenacetin. A recent patent[53] covers the corresponding allyl ether (II.), and its use is indicated in ophthalmological practice.



$$\begin{array}{l}\mathrm{CH_3{\cdot}C{\cdot}NH{\cdot}C_6H_4{\cdot}OEt} \\ \quad\;\| \\ \quad\mathrm{N{\cdot}C_6H_4{\cdot}OEt}\end{array} \qquad \begin{array}{l}\mathrm{CH_3{\cdot}C{\cdot}NH{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH_2} \\ \quad\;\| \\ \quad\mathrm{N{\cdot}C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH{:}CH_2}\end{array}$$

I. $\qquad$ II.

Hypnotics.—A. W. Dox and L. Yoder have prepared a large number of hypnotics of the barbituric acid type, in which the benzyl group, secondary alkyl groups, and butyl groups are essential features.[54] In the benzyl derivatives the antispasmodic action seen in some benzyl derivatives was absent and the hypnotic effect was accompanied by tetanic symptoms. Ethylbutylbarbituric acid,



has also been examined by P. Carnot and M. Tiffeneau and a comparison made with other unsymmetrical disubstituted barbituric acids.[55] Referred to veronal (diethylbarbituric acid) as 10, the hypnotic powers were as follows, methylethylbarbituric acid 5, ethylpropyl- 20, ethylbutyl- 30, ethylisobutyl- 30, ethylisoamyl- 30, and ethylheptyl- 25. On mice ethylbutylbarbituric acid is more toxic than veronal.

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[48] Ges. für Chem. Ind. in Basel, Swiss Pat. 90,587 ; *J. Chem. Soc.*, 1922, i., 828.

[49] O. Kamm and R. Adams, Can. Pat. 217,486 ; *J. Chem. Soc.*, 1922, i., 828.

[50] O. Kamm and E. H. Volwiler, U.S.P. 1,338,573 ; *J.*, 1922, 877A.

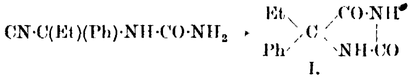
[51] Farbw. vorm. Meister, Lucius u. Bruning, E.P. 161,539 ; *J.*, 1922, 520A ; E.P. 167,781 ; *J.*, 1922, 877A ; E.P. 169,185 ; *J.*, 1922, 997A.

[52] U.S.P. 1,418,900 ; *J.*, 1922, 567A.

[53] Soc. Chem. Ind. in Basle, U.S.P. 1,384,637 ; *J.*, 1922, 520A.

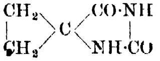
[54] *J. Amer. Chem. Soc.*, 1922, **44**, 1141 ; *J.*, 1922, 518A.

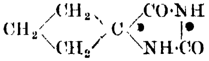
Nirvanol (I.), the best known hypnotic of the hydantoin type, has been synthesised by W. T. Read,[56] starting from phenylethylketone, which combines with ammonia and hydrocyanic acid, yielding phenylethylaminoacetonitrile, $CN.C(Et)(Ph)NH_2$. This is then caused to react with potassium cyanate, the nitrile of phenylethylhydantoic acid formed undergoing internal condensation on boiling with hydrochloric acid:


$$CN{\cdot}C(Et)(Ph){\cdot}NH{\cdot}CO{\cdot}NH_2 \rightarrow \begin{matrix}Et\\Ph\end{matrix}{>}C{<}\begin{matrix}CO{\cdot}NH\\ |\\ NH{\cdot}CO\end{matrix}$$

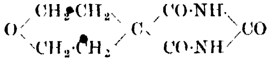
I.

Two *spiro*hydantoins have been prepared by J. F. Thorpe, C. K. Ingold, and S. Sako,[57] but their hypnotic properties are not recorded.

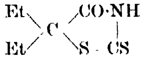

$$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}{>}C{<}\begin{matrix}CO{\cdot}NH\\ |\\ NH{\cdot}CO\end{matrix}$$


$$CH_2{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}C{<}\begin{matrix}CO{\cdot}NH\\ |\\ NH{\cdot}CO\end{matrix}$$

A related *spiro*-compound obtained by condensation of $\beta\beta^1$-dichloro-ether with malonic ester and subsequent condensation with urea was, however, inactive.[58]


$$O{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}C{<}\begin{matrix}CO{\cdot}NH\\CO{\cdot}NH\end{matrix}{>}CO$$

A sulphur analogue, diethylrhodanine,


$$\begin{matrix}Et\\Et\end{matrix}{>}C{<}\begin{matrix}CO{\cdot}NH\\ |\\ S\cdot CS\end{matrix}$$

of the new type of hypnotic described in last year's report has a narcotic action somewhat greater than veronal. Owing to its low solubility in water and its non-absorption when given by mouth, it has no practical value.[59]

SWEETENING AGENTS.

Out of the vast array of data that has been amassed on the relation between chemical constitution and physiological action there are but one or two generalisations of value, and these must be applied with caution. The first is that similarity of molecular build, arrangement, or structure, and hence similarity of localisation in the living tissues, determines similarity of physiological action. The second, the corollary of the first, is that complete dissimilarity of molecular build does not necessarily preclude similarity of physiological action. It is a fairly easy matter to demonstrate the application of these generalisations in a variety of physiological effects, *e.g.*, odour, narcotic action, blood pressure, antiseptic power, etc.

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[55] *Comptes rend.*, 1922, **175**, 241; *J.*, 1922, 685A.

[56] *J. Amer. Chem. Soc.*, 1922, **44**, 1746; *J.*, 1922, 783A.

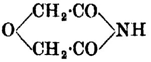
[57] *Chem. Soc. Trans.*, 1922, **121**, 1177.

[58] O. Kamm and J. H. Waldo, *Amer. Chem. Abst.*, 1922, **16**, 408.

[59] *J.*, 1922, 915A.

Sweetness is a physiological property which is readily examined and conforms to these generalisations. A number of interesting substances have been prepared with a view to improvements on the known sweetening materials, with, however, little success. C. Speckan has chosen the dulcin group for variation.[60] Dulcin has the formula $NH_2.CO.NH.C_6H_4.OEt$, is intensely sweet, and the sweetness is retained in $NH_2.CO.NH.C_6H_4.OCH_2.CH_2Br$, and to a slight extent in $NH_2.CO.NH.C_6H_4.O.COC_6H_5$. Replacement of the bromine atom by basic groups gave tasteless substances, as did replacement of the end methyl group in dulcin by the acetyl or benzoyl group. Similarly substitution of the whole ethyl group in dulcin by $-COOEt$ or $-CONPh_2$ gave tasteless substances. In *β*-hydroxypropyl-*p*-carbamidophenyl ether, $NH_2.CO.NH.C_6H_4.O.CH_2.CH.CH_2.OH$, however, a faint sweet taste was noticeable. P. Hermann has likewise devoted some attention to variation of the dulcin molecule without, however, producing any new sweetening agents.[61]

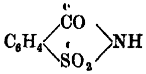
A group of sweet substances which excite the attention are the cyclic imide-ethers of diglycollic acid described by M. Sido.[62] Diglycollimide,



$$O\left\langle\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}\right\rangle NH$$

is tasteless, but its N-alkyl derivatives increase in sweetness from methyl to propyl, its N-aryl are almost tasteless, and the *iso*butylimide bitter. R. Anschütz and S. Jaeger have also prepared some N-arylimides of the same substance with similar results.[63]

The modifications of saccharin,



$$C_6H_4\left\langle\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH$$

are many. Unlike diglycollimide, the parent substance is sweet, its

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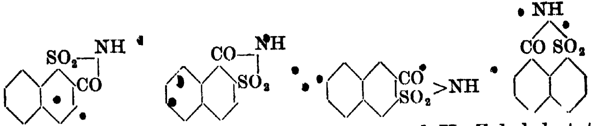
[60] *Ber. deuts. Pharm. Ges.*, 1922, **32**, 83 ; *J.*, 1922, 434A.

[61] *Annalen*, 1922, **429**, 163 ; *J.*, 1922, 915A.

[62] *Ber. deuts. Pharm. Ges.*, 1921, **31**, 118 ; *J.*, 1921, 367A.

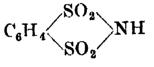
[63] *Ber.*, 1922, **55**, 670 ; *J. Chem. Soc.*, 1922, i., 428.

N-alkyl derivatives are devoid of sweetness. Four naphthasaccharins



have been prepared by H. P. Kaufmann and H. Zobel, but they have all a pronounced bitter taste.[64]

Benzenedisulphonimide,



$$C_6H_4\left\langle\begin{matrix}SO_2\\SO_2\end{matrix}\right\rangle NH$$

has a sweet and acid taste, followed by a bitter taste.[65] *p*-Chlorosaccharin[66] has a bitter sweet taste, whilst 5-chlorosaccharin has a sweet taste,[67] with an intense and persistent bitter after-taste. 6-Chlorosaccharin is more than one-half as sweet as saccharin, but has a somewhat astringent taste.[68]

Much attention is still being devoted to the oxidation of *o*-toluenesulphonamide, $CH_3.C_6H_4.SO_2NH_2$ to saccharin. A. W. Pamfilow oxidised the sodium salt of the amide with 2·4 molecules of potassium permanganate for 6 hrs. at 60°, and claims an 80% yield of saccharin.[69] Others carry out the oxidation with chromic acid in 50% sulphuric acid[70] below 75°, or in 35% sulphuric acid or stronger in the presence of iron, chromium, or manganese salts.[71] Electrochemical methods were patented early in the development of saccharin, and a variant has recently been described whereby a 75% yield of saccharin is obtained by anodic oxidation at 60° in 2*N* solution of sodium carbonate, with a current of 12 volts and a density of 0·04 amp. per sq. cm.[72] The cell is fitted with a platinum gauze anode and a rotating lead cathode.

PUNGENT PRINCIPLES AND DERMATITANTS.

The pungent principle of capsicum or cayenne pepper was shown in 1919 by A. Lapworth and F. A. Royle,[73] and more especially by

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[64] *Ber.*, 1922, **55**, 1499 ; *J.*, 1922, 608A.

[65] A. F. Holleman, *Rec. Trav. Chim.*, 1921, **40**, 446 : *J.*, 1921, 527A.

[66] Fränkel, "Arzneimittelsynthese," 4th ed., p. 147.

[67] J. H. Gerver, *Amer. Chem. Abst.*, 1922, **16**, 1572.

[68] W. Davis, *Chem. Soc. Trans.*, 1921, **119**, 876.

[69] *J.*, 1922, 783A.

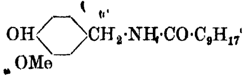
[70] Monsanto Chem. Wks., U.S.P. 1,366,541 ; *J.*, 1921, 195A.

[71] Soc. Chim. des Usines du Rhône, E.P. 153,520, *J.*, 1921, 26A ; E.P. 165,438, *J.*, 1922, 483A.

[72] H. Löwe, E.P. 174,913, *J.*, 1922, 686A. F. Fichter and H. Löwe, *Helv. Chim. Acta*, 1922, **5**, 60 ; *J.*, 1922, 195A.

[73] *T.*, 1919, 843A.

E. K. Nelson,[74] to be the vanillylamide of an unsaturated acid, decenoic acid, with a branched side-chain,



Later in the same year Nelson prepared a series of amides from vanillylamine and various acid chlorides.[75] The amides of fatty acids lower than *n*-hexoic acid had little or no pungency, but above this the pungency increased rapidly to a maximum at the nonoamide, and then fell off with higher members. An interesting extension of this work has been made by E. Ott and K. Zimmermann,[76] who confirm the observation that acids with nine, ten, or eleven carbon atoms produce the most pungent amides. The pungency is, moreover, not dependent to any extent on the position of an unsaturated linkage in the acid, although the presence of such a linkage is necessary for producing pungency in the higher members. Thus the pure vanillylamide of stearic acid is tasteless, whilst that of oleic acid is intensely pungent. By modifying the amine it is shown that the presence and orientation of the methoxy group and of the hydroxyl group are essential features; the amine must be of an aliphatic type.

It is not without significance that spilanthol, the pungent principle of Para cress, is also an amide of an unsaturated fatty acid. Y. Asahina and M. Asano[77] have reduced spilanthol to hydrospilanthol, which is proved by hydrolysis and synthesis to be the *iso*butylamide of decoic acid. Spilanthol is therefore the *iso*butylamide of a decenoic acid, $(CH_3)_2CH.CH_2.NH.CO.C_9H_{17}$, and it is of interest in this connexion that Thoms and Thumen[78] isolated the *iso*butylamide of piperonylacrylic acid, $CH_2O_2 : C_6H_3.CH : CH.CO.NH.CH_2.CHMe_2$, from *Fagara xanthoxyloides*, and J. A. Goodson found it in *Xanthoxylum macrophyllum*.[79]

Piperin, $CH_2O_2 : C_6H_3.CH : CH.CH : CH.CO.NH.C_5H_{10}$, the piperidine amide of piperic acid, may occur to the extent of several per cent. in black pepper, but is not the true pungent principle. E. Ott and F. Eichler now claim to have isolated the active principle chavicin, from pepper resin, as a viscous liquid, which, on hydrolysis yields *iso*chavicic acid, an isomeride of piperic acid, and piperidine.[80] Both *iso*chavicic acid and piperic acid are reducible to the same tetrahydropiperic acid. To the reviewer's mind the evidence of the homogeneity of *iso*chavicic acid is not all that could be desired.

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[74] *J.*, 1919, 654A; 1920, 348A.

[75] *J. Amer. Chem. Soc.*, 1919, **41**, 2121; U.S.P. 1,329,272, *J.*, 1920, 764A.

[76] *Annalen*, 1911, **425**, 314; *J.*, 1922, 77A.

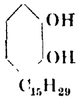
[77] *J. Pharm. Soc. Japan*, 1922, 85; *J. Chem. Soc.*, 1922, i., 505.

[78] *Ber.*, 1911, **44**, 3717; *J. Chem. Soc.*, 1912, i., 115.

[79] *Biochem. J.*, 1921, **15**, 123; *J. Chem. Soc.*, 1921, i., 265.

[80] *Ber.*, 1922, **55**, 2653; *J.*, 1922, 914A.

Certain trees, or extracts therefrom, are known to produce a painful skin disease in susceptible persons. The constituent of Japanese lac responsible for this is urushiol, a catechol derivative with an unsaturated side chain of fifteen carbon atoms.[81]



Experiments on catechol derivatives show that the irritating action increases with increasing length of the side chain, but is not appreciably affected by its position. Lobinol, the dermatitant of the Poison oak, appears to be closely related, as it contains the catechol nucleus and is unsaturated.[82]

ANTISEPTICS.

To the investigator in chemotherapy there are ever present two very formidable barriers. The first is the lack of knowledge as to the mechanism of the action of a drug, the second, the absence of information as to the distribution of residual affinity in the drug, and it is this distribution of residual affinity which determines the selective distribution of the drug in the living tissues. The former hinders the pharmacologist in the correct experimental testing of a series of drugs, whilst the latter prevents the chemist from devising the most efficacious substance, the only alternative at present being the almost haphazard synthesis of numerous new chemical individuals. The no small success which has been obtained by the present methods in various groups of chemotherapeutic substances, has started in each case from some initial observation which has given a lead. We owe Ehrlich and Hata's salvarsan to the observations of Thomas and Breinl, and later of Uhlenhuth and co-workers on the trypanocidal and spirillicidal action of atoxyl, and Bayer 205 to Ehrlich and Shiga's discovery of the trypanocidal action of trypan red. At the present time many such clues, both among organo-metallic compounds and non-metallic organic compounds, are being assiduously followed up by numerous investigators. Success has, so far, only attended the treatment of generalised infections due to protozoal and spirochaetal organisms; generalised bacterial infections cannot at present be checked, although localised bacterial infections respond favourably in some cases to irrigation with suitable antiseptics.

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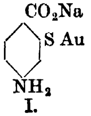
[81] R. Majima, *Ber.*, 1922, **55**, 191; *J. Chem. Soc.*, 1922, i., 265.

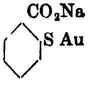
[82] J. B. Macnair, *J. Amer. Chem. Soc.*, 1921, **43**, 159; *J. Chem. Soc.*, 1921, i., 387.

ORGANO-METALLIC COMPOUNDS.

Gold Compounds.—Tuberculosis is a prominent instance of a disease which does not respond to serum therapy. Attention must therefore be paid to other possible curative agents. The possibility of utilising gold compounds as curative agents started from Koch's discovery of the inhibitory action of gold cyanide on tubercle bacilli at a dilution of 1 in 2,000,000. The presence of serum, however, diminishes its potency. Various addition compounds of gold cyanide, chloride, or thiocyanate with organic bases such as hexamethylenetetramine, piperazine, cantharidine in combination with ethylenediamine, choline and hexamethylenetetramine quaternary salts have been protected from time to time, with a view to their use in tuberculosis.[83] Their application, however, has met with little success. In German medical literature frequent reference is made to krysolgan, which is reported on favourably for the treatment of tuberculosis in man.[84] Krysolgan was introduced by A. Feldt,[85] and is described by him as the sodium salt of a complex 4-amino-2-aurophenol-1-carboxylic acid. It contains 50% of gold, inhibits the growth of tubercle bacilli at a dilution of 1 in 1,000,000, and gives a neutral solution. The salt is marketed by the Farbewerke vorm. Meister, Lucius, und Brüning, who have covered by patent some allied substances. By treatment of mercaptobenzenes with double gold chlorides auromercaptobenzenes are formed. The sodium salts of 4-amino-2-auromercaptobenzene-1-carboxylic acid,[86] (I.), and of aurothiosalicylic acid [87] (II.), are specially mentioned,



I.



II.

whilst salts of organic bases, *e.g.*, ethylenediamine, with aurothiosulphuric acid have been protected as therapeutic agents in tuberculosis and syphilis.[88]

No detailed reference need be made here to the addition compounds of arsenicals with gold chloride, as they are well known. The Bayer firm have recently protected the addition products of gold chloride with compounds of the Methylene Blue group.[89]

[83] G.P. 284,234, 284,260, 269,661, 276,134, 276,135, 284,259.

[84] E. Levy, *Deut. med. Woch.*, 1922, **48**, 223.

[85] *Berl. klin. Woch.*, 1917, 1113; 1918, 289, 911; *cf. Münch. med. Woch.*, 1920, 1500; *Lancet*, 1922, 1, 395.

[86] U.S.P. 1,207,284; *J.*, 1917, 163.

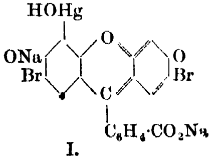
[87] E.P. 157,226; *J.*, 1922, 347A.

[88] E.P. 1869 of 1914; *J.*, 1914, 806.

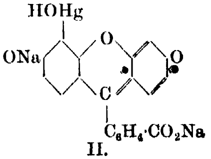
[89] G.P. 347,376; *J.*, 1922, 522A.

The products are stated to be strongly antiseptic against tubercle bacilli, gonococci, and spirochaetes.

Mercury Compounds.—The powerful antiseptic action of certain inorganic mercury compounds is undoubtedly due in the first place to the mercuric ion. The mercuric ion cannot, however, be the sole factor determining the antiseptic properties of organic mercury compounds. In a previous report [90] reference was made to mercurochrome-220 (I.), a mercury compound of dibromofluorescein. Further experience[91] shows that it is a powerful germicide against gonococcus, this bacillus being forty times as susceptible as *B. coli.* It is said to be of value in cystitis, and as a general surgical dressing. An allied compound, flumerin (II.), is the sodium salt of hydroxymercurifluorescein.[92] It has been tried intravenously as an antisyphilitic, but is decidedly inferior to the salvarsans. It is said to eradicate experimental syphilis in the rabbit, and to have proved of value in syphilis in man.



I.



II.

The growth-inhibiting properties of a series of organo-mercuric compounds on tubercle bacilli have been determined by L. M. De Witt.[93] The compounds examined include mercury derivatives of phenol, nitro- and nitroso-phenol, and saligenin, of aniline, nitroanilines, methyl and ethyl derivatives of aniline and nitroanilines. The interesting observation was made that many of these substances exceed phenol or mercuric chloride in potency. Those of the highest inhibitory power are to be tested later, in order to determine their bactericidal and therapeutic efficiency. T. A. Henry and T. M. Sharp have described mercury derivatives of the reactive *ortho-*, *meta-*, and *para*-hydroxybenzaldehydes.[94] The *ortho* and *meta* compounds were the strongest bactericides when tested on *B. typhosus.*

Bismuth, Vanadium, Niobium, and Other Compounds.—Some preliminary results in the treatment of syphilis by sodium potassium bismuthotartrate were noted in last year's report.[95] The work has been carried several stages further during the past year. Other complex bismuth compounds such as ammonium bismuth citrate, sodium bismuth lactate, sodium bismuth sub-gallate, and bismuth oxyiodogallate, have been tried by R. Sazerac and C. Levaditi on experimental syphilis in the rabbit, the conclusion being drawn that a large number of bismuth compounds have a more or less energetic antisyphilitic action, but that, so far, sodium potassium bismutho-tartrate is best.[96] It is superior to mercury and approaches the salvarsans in value. In addition it has the advantage of stability. It cannot, however, be given intravenously with safety. L. Guénot and L. Fournier have tried it on 200 human cases without untoward accident.[97] On trypanosomiasis in mice and guinea-pigs it was not found curative,[98] although it caused the disappearance of *Trypanosoma brucei* in mice.[99]

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[90] *Ann. Repts.*, 1920, **5**, 503.

[91] E. O. Swartz, D. M. Davis, *J. Amer. Med. Assoc.*, 1921, 76, 544; H. H. Young, E. C. White, E. O. Swartz, *ibid.*, 1921, 77, 93.

[92] E. C. White, J. H. Hill, J. E. Moore, H. H. Young, *J. Amer. Med. Assoc.*, 1922, **79**, 877.

[93] *J. Infec. Dis.*, 1922, **30**, 363.

[94] *Chem. Soc. Trans.*, 1922, **121**, 1055.

[95] *Ann. Repts.*, 1921, **6**, 532.

Vanadium, niobium, and tantalum occur in the same group of the periodic law as arsenic, antimony, and bismuth. It is therefore not surprising to find that the complex vanado-tartrates of sodium or potassium have effected cures in syphilitic rabbits. In man the results were also favourable, although not so good as with arsenic or bismuth compounds.[100] This work extends the original observations of Pröscher, Seil, and Stillians, who in 1917 first demonstrated the antisyphilitic action of vanadium.[101] Compounds of niobium and tantalum proved void of antisyphilitic action. Niobium and rhodium were also without beneficial action on mice infected with *Trypanosoma brucei*.[102]

Dyes.—Thanks to the work of numerous investigators there is ample experimental evidence to show that many dyes have a powerful bactericidal action. For the treatment of generalised bacterial infections this is by no means sufficient. The ideal antiseptic or chemotherapeutic agent is one which possesses, *in vivo*, a bactericidal action and is compatible with the forces necessary to the host's defence. In doses non-lethal to the host it should therefore exert a negligible action on phagocytes or stimulate them to activity. Failure to realise these essentials is one cause of the lack of success which has attended attempts to cure diseases due to generalised bacterial infections on the basis of the bactericidal action of dyes, observed, *in vitro*, in aqueous solution.

An account of a praiseworthy attempt to cope with the numerous factors concerned in evaluating an antiseptic for internal use has been published[103] in America by L. D. Felton and K. M. Dougherty, who have determined the organotropic, bacteriotropic, and leucocytotropic action of a number of dyes and cinchona derivatives. The organotropic action was measured by the maximum dose tolerated by mice, the bacteriotropic action by the bactericidal action on *Staphylococcus aureus* in whole blood, and the leucocytotropic action by the inhibition of phagocytic action towards staphylococci in serum. As a rule, in the triphenylmethane bases, in safranines, phenazines, quinones, and the cinchona group the deleterious action of the drug was greater on the leucocyte than on the bacteria or on the host. In an *in vivo* experiment therefore an interference with the host's natural defensive forces might be expected. *p*-Methoxymalachite Green, Ethyl Violet, and Proflavine approached the condition where a tolerated dose for mice was staphylotropic but not leucocytotropic. The account promised later, of the influence of these drugs on an experimental pneumococcus infection in mice will be looked forward to with interest.

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[96] *Ann. Inst. Pasteur*, 1922, **36**, 1.

[97] *Ibid.*, 1922, **36**, 14.

[98] S. Adler, *Ann. Trop. Med. Parasit.*, 1921, **15**, 438

[99] A. Frouin and M. Guillaumie, *Comptes rend. Soc. Biol.*, 1921, **85**, 466.

[100] L. Fournier, C. Levaditi, and A. Schwartz, *Comptes rend. Soc. Biol.*, 1922, **87**, 23.

[101] *Amer. J. Syp.*, 1917, **2**, 347.

[102] A. Frouin and M. Guillaumie, *Comptes rend. Soc. Biol.*, 1921, **85**, 466.

The bactericidal action on fourteen strains of bacteria, in broth, of about 80 coal-tar dyestuffs has been determined by T. H. Fairbrother and A. Renshaw in an attempt to correlate chemical constitution and bactericidal action.[104] In general they find, like other observers, that amino-groups are important factors in the development of antiseptic action, but their effect may be diminished or annulled by the presence in the molecule of groups such as nitro, carboxyl, sulphonyl, or naphthylamino or by a loading of the amino-groups by alkyl substituents. The lethal dose of about 40 dyes was also determined on paramœcia as representative of protozoa. The selective action, however, of a series of compounds for various organisms is a well-known phenomenon and precludes the application of results obtained with paramœcia to other protozoa. A striking instance of this selective action was recently recorded by J. B. Cohen, C. H. Browning, and R. Gulbransen, who, in addition to the discovery of the powerful antiseptic action of the cyanine dyes, Sensitol Red, Green, and Violet—used commercially as photographic sensitisers—found[105] that the ratio of the lethal concentration of Sensitol Red for *B. coli* and *Staphylococcus aureus* was probably greater than 2000 : 1.

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[103] *J. Exp. Med.*, 1922, **36**, 163.

[104] *J.*, 1922, 135T.

[105] *Brit. Med. J.*, 1922, **1**, 514 ; *Nature*, 1922, **109**, 750.

PHOTOGRAPHY.

By Raymond E. Crowther, A.I.C.

The photographic industry, in common with most of the other industries which come within the purview of these reports, has continued to feel the "slump" effects of after-war fatigue and readjustment during the past year. A review of the situation, however, cannot fail to awaken surprise that in this branch of industry, which hitherto has been regarded by the majority of the community as a pure luxury trade—it is even so classified by the German Government—the slump conditions have been so lightly felt in this country. One can conclude from this fortunate circumstance that photography has filled a gap in the aesthetical life of the "average" man and that, apart altogether from the enormous powers it places in the hands of the pioneers of modern science, whose discoveries will in all probability be vital factors of communal life in the not far distant future, it is coming to be recognised as an educational necessity. This could not have been so if the apparatus and materials incidental to the art or science of photography had not already attained a uniformity of quality, and maintained it in such a measure as warrants the production of successful results with little wastage.

Nor is it only in the peaceful existence of a community that photography has come to be regarded as a non-luxury: all the unfortunate participants in the late European catastrophy apprised it at its true value, and it is consequently regarded by several Governments as a "key" industry, the fostering and protection of which is a matter of national import.

The impetus given to the industry in Germany, where the rapid decrease in the international value of the currency has enabled extraordinarily low costs of production to be maintained, has been a serious menace to home manufacturers, who in May and June made complaints before a committee of the Board of Trade[1] with a view to securing an increased measure of protection.

Whilst the existing import duties on practically all the apparatus and material used in photography are not effective in preventing their importation and subsequent sale at competitive prices, it is doubtful whether an increase would allow of a greater margin of profit per article or a greater aggregate of profit per annum to home manufacturers for, with a disciplined working community such as exists in Germany, the currency could be further depreciated, if necessary, with a consequent repetition of the "complaint."

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[1] *Brit. J. Phot.*, 1922, **69**, 298, 342, 371.

That the home photographic industry must be retained cannot be gainsaid, but the problem of its retention is undoubtedly an involved one, which cannot be completely solved by tariff regulations and in which one of the most important factors is the less expensive existence of the German producer.

The adoption of a pessimistic view, however, would be unwarranted for, on the one hand, the home-produced materials, and particularly the sensitive materials, maintain unimpaired the high standard of quality for which they have been justly renowned and are in steady demand on such of the world's markets as are open to competition; and, on the other hand, an increasing amount of valuable research is being undertaken which is bound to be of importance in the near future. This latter asset is probably of greater moment than would at first sight appear. On the Continent, the effect of the financial topsy-turvydom is felt most by that section of the community from which the scientific workers are recruited, and all efforts to maintain the former level of scientific education are proving insufficient to cope with the situation. In Austria, the general depression is evinced by the disappearance from circulation of the well-known journal *Photographische Korrespondenz.*

In Germany also the substitution of a fortnightly issue of *Photographische Industrie* for the former weekly issue is the straw which indicates the direction of drift.

In Switzerland however, the appearance of a new monthly magazine, *Camera,* is to be noted. The publication of this magazine, in which contributions by such workers of note as Lüppo-Cramer, König, etc., occur, serves to indicate that countries with normal currency are likely to command the best brains of Europe—a truism which in the light of recent advances in the exchange value of English currency should afford our industrial leaders a considerable amount of satisfaction. The publication in abridged form of the Communications which have been made during the years 1919-1920 by the Eastman Research Laboratories to various societies and journals, and the proposed issue as a separate volume of *Science, Technique et Industrie Photographique,* published hitherto as a supplement to the *Revue Française de Photographie,* in that they serve to indicate the demand for scientific photographic literature, are worthy of mention.

KINEMATOGRAPHY.

During the past year much has been heard from the proprietors of kinematograph theatres of the adverse effects of the entertainment tax on the volume of patronage, but it would be better to make a careful analysis of the situation, considering all the contributory factors, than blindly to attribute the undoubted falling off of the public's appreciation to a factor which has had little deterrent influence on other types of audience or spectators. The present "slump" affords a good opportunity for stocktaking, and a review of the situation indicates that the past phenomenal popularity of the kinema was due partly to novelty and partly to the fact that this novelty appealed to a section of the community which had not been educated to amuse itself in its leisure time. So long as the appearance of novelty could be maintained and so long as this particular section of the community had the means to pay for its amusement, for just so long have the "pictures" been popular.

The time appears to have arrived, however, when the kinema must appeal to the "average" intellect and successfully compete on its merits with various counter attractions of a higher order of intellectuality if its prosperity is to continue.

The introduction of more or less sordid drama by means of "animated photography" to hundreds of thousands all too eager for such excitement and hitherto only able to procure it at the expense of depriving themselves of desirable company—namely, by reading—constituted no doubt all-sufficient reasons for the initial success; but sooner or later the communal value of the industry, that is to say, its value as a factor in the uplifting of a community, must become its life and death factor. It cannot be reasonably argued that at present the average programme is worth the time which an ordinary middle-class individual has to spend in order to sift out the little worth seeing from the enormous bulk of worthless and anti-social material therein.

Until the kinema becomes the rendezvous of the people who matter in the intellectual life of the community, until it is really fit to place before the children of this generation who are to be its mainstay in the next, it can only hope at best to enjoy short periods of financial prosperity interspersed with much longer periods of "bad times."

Although these comments may appear somewhat incongruous, it need only be pointed out that the continued existence of the photographic industry is very largely bound up with the keeping alive of that section of it which consumes the major portion of its products, viz., kinematograph films. No apology is offered therefore by the writer for having considered the subject from the social aspect.

A further fact must not be overlooked, namely, that in the past kinematography has been severely handicapped, so far as the patrons are concerned, by the inability to convey impressions by means of speech—the alternation of titles with long drawn out "close ups" rapidly become somewhat irksome to watch. It is a poor substitute, which before long will very probably be displaced by the "talking" film. In fact, towards the latter end of 1922 a successful public demonstration of speaking film pictures was given in Berlin.[2] The various operations for sound reproduction in this particular instance are protected by patents granted to H. Vogt, J. Engl, and J. Massolle,[3] and include a novel form of sound-light intensity converter, which depends upon the conductivity of the ionised atmosphere surrounding an electrically charged wire. The movements of the sound-operated diaphragm are registered as strips of varying opacity, which form a ladder design along the edge of the picture film. Perfect synchronisation of picture and sound is thus achieved when the light intensity to sound conversion is made by the now well-known selenium cell apparatus. The inventors are to be congratulated on their success, but it is doubtful whether the existing vested interests will welcome the improvement. Its adoption would mean the installation of new delicate and expensive apparatus and would necessitate drastic changes in "producing" methods. It would mean, for example, that the "actor" would have to rely on his own skill and that the "producer" would become dumb. It would necessitate the introduction of refinements comparable with those pertaining to the theatre stage, and although it would eventually enable the kinema to take its place amongst the arts, the transition from the present state of affairs could only be slow. It may be anticipated therefore that the inventions in the "speaking film" field[4] will not prove epoch-making.

The case of stereoscopic projection, with which inventors continue to concern themselves,[5] is in a somewhat different category, since not only will the unnatural perspective, which is all too evident when the subject includes near foreground and relatively important background objects, disappear, but, in addition, no modification of the existing "production" technique would be necessitated and but slight alteration of apparatus would be called for unless synchronised viewing devices for each spectator are essential. The illusion of stereoscopy which results from correct displacement of the camera during taking has already been made use of with some amount of success, and W. H. Merrill and T. C. Martin[6] have secured a patent for means of imparting the necessary movement to the camera.

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[2] *Phot. Rund.*, 1922, 266.

[3] E.P. 157,433, 157,440, 157,443–4.

[4] A. O. Rankine, *Nature*, 1921, **108**, 276. P. M. G. Toulon, E.P. 522,527. *Rev. Franç. Phot.*, 1921, **2**, *Suppl.*, 103. R. Mylo, E.P. 149,206–7. E. Viola, *Atti Accad. Lincei*, 1921, **30**, II., 416.

[5] J. Brizon, F.P. 520,908, 522,999. A. Boorman, E.P. 165,587. L. D. Williams, E.P. 173,833.

It must not be forgotten, however, that the mere alteration of the relative positions of the actors imparts a measure of stereoscopy to most scenes, and the impression of depth which true stereoscopic projection would introduce would, perhaps, scarcely be noticeable.

The many drawbacks attendant on the present discontinuous nature of the film movement in both "taking" and projection are too well known to need emphasis, and it is not surprising therefore that much work is being carried out with a view to perfecting continuously moving film apparatus.[7] The perfection of such apparatus will add enormously to the value of the kinematograph in its application to the analysis of motion, and would enable many types of subjects to be recorded which at present have to be passed by. Further, a noticeable decrease in the cost of production should result from the longer life of a film continuously projected, and the audiences of the smaller halls, which have suffered much more during the present depression than those where other attractions form part of the programme, would receive their reels in a much less abridged form than is at present the case. The assistance which the continuously moving film would give to those working on the speaking film will be apparent from a perusal of the account of Vogt, Engl, and Massolle's work.

There are unmistakable signs of a revival of interest in home kinematography, a natural result, perhaps, of the steady extension of electric lighting facilities. The introduction of the kinematograph into the homes of the people is largely bound up with the supply of suitable "non-inflammable" film base, for although all the regulations which govern public exhibitions might not be relaxed if nitrocellulose were displaced by the much less inflammable esters, there can be no doubt that the householder and probably his fire insurance company also would take more kindly to a less inflammable material. There does not appear to be any necessity, however, for such a truly non-inflammable material as the band of aluminium which has been produced by K. Weiss,[8] and whilst it is obvious that both sides of such a "film" may be used for carrying pictures there is not much likelihood of its replacing the ordinary transparent variety. Acetate film has entered the field, and is now being fairly extensively used in the production of positives. From all points of view it is to be regretted that acetate base is not suitable for negative film making—and so far it has not proved to be inert towards the modern high-speed emulsion—because only a part of the advantages it would otherwise afford can be turned to account. So long as nitrate base has to be used in negative work, the manufacturing and storage fire risks remain. These risks are at least as important as those appertaining, under the present regulations, to the exhibiting of such film, and although the action of the French Government in prohibiting after July, 1924, the public exhibition of pictures on nitrate film is a step in the right direction, it is doubtful whether much public benefit will result. The relative instability of acetate film precludes its use for record purposes, even when it is desired to preserve positives only, and in addition its anti-wear qualities leave much to be desired. Attempts are being made to perfect viscose film and to incorporate therein the sensitive salts.[9] Should success be achieved, the low cost of this product will guarantee a ready market. Moreover, the protection of the picture image resulting from the absence of a separate emulsion film would be an important asset.

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[6] W. H. Merrill and T. C. Martin, E.P. 175,912. E. B. Moore, U.S.P. 1,396,651. A. Polak, F.P. 528,184, and Additions 23,945, 24,071.

[7] J. Szczepanik, E.P. 148,254, 155,764. C. Zeiss, E.P. 149,280, G.P. 350,194. E. Mechau, E.P. 152,347. A. A. Thornton, E.P. 171,515. C. F. Jenkins, U.S.P. 1,385,325. O. Messter, G.P. 336,649. K. Higginson, E.P. 179,648. M. F. and L. D. Hill, U.S.P. 1,407,535. Ernemann-Werke A.-G., G.P. 348,936. W. Heape and H. B. Grylls, E.P. 178,472. H. Grubb, E.P. 178,474.

[8] *Phot. Ind.*, 1922, 311.

It will be apparent from the foregoing that substitutes for the nitrate film are receiving the serious consideration of film manufacturers, and it is to be anticipated that, with the extension of the knowledge of cellulose and its derivatives, the day is not far distant when nitrogen-bearing esters will have ceased to be the basis of kinematograph or other photographic film.

COLOUR PHOTOGRAPHY.

The public exhibition during the past year of the Prizma natural colour film referred to in last year's Report (p. 546) has afforded an opportunity of comparison with the results of earlier processes. Unfortunately it cannot be said that the newer process showed striking improvement over the now obsolete kinemacolor results; indeed the latter, in spite of its well-known colour-fringe drawback, gave distinctly more harmonious rendering and dealt with the more difficult lighting effects more efficiently. Perhaps the producers of the Prizma pictures have been too ambitious, have not realised the limitations of their process, or were not familiar with the correct lighting conditions for some of the scenes portrayed, but whatever may be the causes one is not very impressed by the amount of progress made in this branch of colour photography during the last decade as evinced by the exhibition of *The Great Adventure.* Of other dye toning processes at present receiving attention it is of interest to note that a company has been formed in Germany to exploit Traube's patents in kinematography.

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[9] La Cellophane, F.P. 519,863. See also J. E. Brandenburger, *J.*, 1922, 524A.

Gaumont's three-colour additive process, which is being successfully and regularly worked by its inventor, has been improved as to projection operation by the perfection of registration mechanism which may be manually or automatically controlled. This process represents, in the writer's opinion, the greatest achievement so far obtained in colour kinematography by additive methods—the entire absence of colour fringes is noteworthy, as is also the faithfulness of the colour rendering. This latter quality is to be expected of a three-colour process. For subjects in a high key, however, the introduction of a plain black and white component would appear to be desirable. The importance of this black and white component is recognised in the patent of R. O. P. Humphrey and C. H. Friese-Greene,[11] who obtain it by a novel construction of filter shutter. An example of a "patterned" additive process is represented in the patents of A. Keller-Dorian,[12] who obtains the screen pattern by refraction elements on the unsensitised side of the film, and so arranges a three-sectioned three-coloured diaphragm that each element forms an image of each of the colour filters on the sensitive emulsion. The negative is converted by the well-known reversal process into a positive, and projection ensues through an apparatus the optical and colour members of which are identical with those of the "taking" apparatus. In common with many other colour processes as applied to kinematography, the drawback of necessitating special projection apparatus is present, although in this case the special apparatus can be relatively easily applied to existing projectors. Many workers whose judgment is of importance in these matters, express the opinion that a *sine qua non* of the financially successful colour film is the presence of the colour in the film, a circumstance allowing of the use of the ordinary projector. The Eastman Kodak Co. appear to be bringing their Kodachrome process on to a commercial basis and have obtained a patent for a means of securing registration of the two-coloured images which occupy superposed areas on either side of double-coated film.[13]

Of colour processes not primarily applicable to kinematography that of L. Dufray[14] is of interest as being similar to the Paget process for the production of natural coloured positives, whilst that

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[10] Etabl. Gaumont, F.P. 525,883, 527,139, and Addition 23,941, and F.P. 533,812.

[11] E.P. 183,150.

[12] F.P. 521,533.

[13] J. G. Capstaff, U.S.P. 1,394,504.

[14] F.P. 520,784.

of J. B. E. Didier[15] recalls the earlier "Pinachrome" attempts of E. König.

The patents granted to E. A. Lage[16] and E. Wolff[17] represent attempts to utilise fully the differential or selective colour-sensitising powers of modern photographic colour-sensitisers. This section should not be closed without making reference to the publication of E. J. Wall's "Practical Colour Photography," a comprehensive volume in which are to be found reliable descriptions of and working instructions for all processes of colour photography which have reached a commercial stage.

SENSITISING AND DESENSITISING.

Work on the isocyanine and allied sensitisers has been continued by W. J. Pope and his collaborators, and our knowledge of the characteristics of many useful dyes is increasing. The absorption spectra and the sensitising effect of various substituted 1.1′-dimethylisocyanine iodide derivatives referred to in last year's report (p. 549) are illustrated in the *Photographic Journal*,[18] and important generalisations concerning the relation of the constitution of the substituents and the optical and photographic properties are made. W. T. K. Braunholtz[19] has shown that of the isomeric 5.5′-, 6.6′-, 7.7′-diethoxy-1.1-diethylcarbocyanines, the 6.6′ confers the greatest and the 5.5′ the least red sensitiveness. As is the case with the derivatives prepared by Miss Hamer, the characteristic sensitising maxima are nearer the red end of the spectrum than the absorption maxima.

W. H. Mills[20] has described the preparation of thiocyanine and carbothiocyanine dyes of analogous constitution to the iso- and carbo-cyanines respectively and found that they exhibit characteristic sensitising properties.

Some interesting observations on the technique of sensitisation by bathing, and on the properties of emulsions sensitised by bathing, are made by F. M. Walters, jun. and R. Davis.[21] Although much of the information contained in this paper is not new, it has not been generally available and its publication should serve a useful purpose. It should be considered in conjunction with E. Stenger's communications[22] on the keeping qualities of sensitised emulsions. The relative instability of emulsions sensitised by "bathing" as compared with those "emulsion" sensitised is eloquently testified to by Stenger's results, and for the present at least it may be assumed that those methods of procedure which yield the most highly sensitive products induce a corresponding instability and fogging tendency. This assumption is supported by the remarks accompanying the details of procedure of "hypersensitising" autochrome plates published by F. Monpillard.[23]

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[15] F.P. 524,143.

[16] E.P. 183,189; *J.*, 1922, 729A.

[17] G.P. 345,734; *J.*, 1922, 567A.

[18] F. M. Hamer, *Phot. J.*, 1922, **62**, 8; *J.*, 1922, 120A.

[19] *Chem. Soc. Trans.*, 1922, **121**, 169; *J.*, 1922, 198A.

[20] *Ibid.*, 455; *J.*, 1922, 465A.

[21] *U.S. Bur. Stand. Sci. Papers*, No. 422, 1921, **17**, 353; *J.*, 1922, 960A.

[22] *Z. wiss. Phot.*, 1922, **21**, 246; *Phot. Ind.*, 1922, 835, 859, 878, 898; *J.*, 1922, 440A.

A sensitising dye, 2-*p*-dimethylaminostyrylpyridine methiodide, possessing similar properties to König's Pinaflavol, has been prepared by W. H. Mills and W. J. Pope[24] by boiling in alcohol *p*-dimethylaminobenzaldehyde with α-picoline and piperidine, and the same workers with J. E. G. Harris[25] describe an improved method of separating isoquinoline in a pure state from coal tar quinoline, the preparation and properties of Isoquinoline Red and its 6′-methyl and 6′-ethyl derivatives.

The influence of the introduction of bromine into the nucleus of the molecule of Pinacyanol has been investigated by K. L. Mondgill[26] who finds that the halogen considerably depresses the sensitising powers of the dye and causes a shift of the maximum towards the red end of the spectrum. Some new sensitisers for the deep red are the subject of a communication by C. E. K. Mees and G. Gutekunst.[27] The acetaminocyanol appears to be different from the compound previously described by Pope and sensitises quite differently according to whether it is applied in the emulsion or by bathing. Kryptocyanine (*Ann. Repts.*, **6**, 105), is stated to be the most powerful sensitiser known and gives a maximum at $\lambda = 7600$.

Lüppo-Cramer has continued to work on the increase of general sensitiveness by dyes[28] and has come to the conclusion that emulsions in which nuclei exist as a result of ripening may be further sensitised to white light by the action of appropriate dyes. The appropriateness of the dye may be the completely decisive factor, as the work of E. König and R. Schuloff[29] indicates a very close relationship between the chemical constitution of the dye and its behaviour. Their work has led them to the conclusion that simple alteration of a substituent radicle may convert a sensitising dye into a desensitising dye. Unfortunately these authors do not find themselves able to disclose details of the constitution of the dyes which behaved in this manner and the difficulty of forming any conception of the mechanism of sensitisation and desensitisation remains, but in view of the known shift in the position of the maximum sensitisation which modification of the substituent causes, it is not impossible that desensitisation is a species of sensitisation, the maximum being shifted beyond the confines of the visible spectrum. Lüppo-Cramer maintains his contention that desensitisation is an oxidation phenomenon,[30] and amongst other items of evidence in support of this statement he cites the fact that desensitisation reduces the sensitiveness of an emulsion to X-rays, whereas optical sensitisers impart no increased sensitiveness to X-rays. A. Steigmann[31] interprets the results of experiments in which exposed plates were treated with mercuric salts before development as being in accord with the oxidation theory of desensitisation. The suggestion is made that the desensitiser is absorbed by the silver halide of the emulsion which is thus isolated by a sheath of oxidising environment. It might legitimately be deduced from this hypothesis that desensitisers would have in every case an inhibitory or retarding effect upon the development process, whereas as a matter of fact in many instances the opposite, *i.e.*, an acceleration of development, is found to result from desensitisation.[32] A theory which does not necessitate any absorption-complex isolation assumption is suggested by Lüppo-Cramer,[33] who assumes that the nuclei of nascent silver react with the dye in the same way as does zinc dust—all known desensitisation dyes are reducible with zinc dust whilst sensitising dyes are not—and are thus deprived of their characteristic sensitising properties. This theory certainly appears attractive and should stimulate Lumière and Seyewetz to repeat their washing experiments, in which they found a gradual return of sensitiveness as the washing proceeded, introducing the modification of using de-oxygenated water. Whatever theory may come to be generally accepted, however, the practical utility of the desensitisation process is an established fact and the introduction of Pinakryptol and Pinakryptol Green[34] has simplified the manipulation. Patents have been secured in Germany[35] for desensitising plate backings and in this country the Imperial Company has during the past year placed on the market a plate carrying such a backing. As has already been pointed out by the writer such backings are not novel. A somewhat surprising statement to the effect that Phenosafrainine reduces the natural sensitiveness of silver bromide to blue and violet only to one-fortieth of its normal value is made by C. Bonacini[36]; this does not accord with the observations of earlier experimenters. Lumière and Seyewetz,[37] for example, as the result of spectral measurement state that in the blue region, with a maximum depression about 425$\mu\mu$ the sensitiveness falls to 1/750 of its original value. The recognition of the undoubted residuum of sensitiveness in the blue is of importance as it governs the choice of the illuminant in which desensitised emulsions are handled. Appropriately enough the old batswing gas flame was used in connexion with tests of the first desensitiser of which we have a record. This was as early as 1885 and the desensitiser was the well known and then largely used developer "ferrous oxalate."[38] The absence of a sulphite from this developer, coupled with the fact that a sulphite prevents the formation of desensitising products in the oxidation of aminophenolic developers, somewhat strengthens the case for the oxidation theory.

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[23] *Bull. Soc. franc. Phot.*, 1922, **9**, 90; *J.*, 1922, 484A.

[24] *Chem. Soc. Trans.*, 1922, **121**, 946; *J.*, 1922, 594A.

[25] *Ibid.*, 1029; *J.*, 1922, 581A.

[26] *Ibid.*, 1509; *J.*, 1922, 838A.

[27] *Brit. J. Phot.*, 1922, **69**, 474; *J.*, 1922, 689A.

[28] *Phot. Ind.*, 1922, 238.

[29] *Phot. Korr.*, 1922, **59**, 43.

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[30] *Phot. Ind.*, 1922, 287

[31] *Loc. cit.*, 1921, 71 ; 1922, 469.

[32] Lüppo-Cramer, *Phot. Ind.*, 1922, 405. R. E. Liesegang, *ibid.*, 601.

[33] *Ibid.*, 774–775.

[34] *Brit. J. Phot.*, 1922, **69**, 351, 353 ; *J.*, 1922, 567A.

[35] K. Wiebking, G.P. 354.432 ; *J.*, 1922, 730A. *See also* M. Schiel, *Phot. Rund.*, 1922, **59**, 185. H. Meissner, *ibid.*, 233. H. Schreiber, G.P. 350,658, *J.*, 1922, 729A.

The last item of interest under this heading is the observation of the inhibition of desensitising action by certain "filter" dyes—notably Tartrazine—which are added to the emulsions of the so-called self-screened orthochromatic plate during manufacture.[39] Fortunately this inhibition is not serious under normal conditions and is not at all apparent when the desensitiser (Phenosafranine) is mixed with the developer. According to Lüppo-Cramer Rapid Filter Yellow (Hoechst) does not exhibit this antagonistic action.

DEVELOPMENT.

The communications of theoretical importance which have appeared include one or two which the research worker cannot afford to neglect. The first deals with the work of T. Otashiro,[40] who investigated the uniformity of development of plates treated whilst held in a rotating holder immersed in the solution. Under these conditions it was proved that development was far from being uniform—indeed, when rotation is omitted the results showed a noticeably higher order of uniformity. The lack of uniformity is partly ascribed to currents of specifically heavier or lighter development products, the formation of which has been already demonstrated by E. R. Bullock.[41]

A second communication by O. Bloch[42] deals with the same subject. It is shown that with dish development no matter what type of rocking be resorted to it is impossible to secure uniform development unless some device such as a roller squeegee be passed in two directions at right angles over the surface of the plate during the operation. The writer, when working with W. F. A. Ermen on the subject of the activity of developing agents, was led to abandon the use of glass plates because of these difficulties in ensuring uniform development. By using flat film curled emulsion side inwards in a porcelain beaker and periodically pouring off the solution and pouring back again uniform development was secured.

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[36] *Il Prog. Fot.*, 1921, **28**, 210.

[37] *Brit. J. Phot.*, 1921, **68**, 371.

[38] H. Bäckström, *Phot. Rund.*, 1922, **59**, 181. Lüppo-Cramer, *ibid.*, 202.

[39] *Phot. Ind.*, 1921, 912, 1022.

[40] *Bull. Kiryu Tech. Coll.*, January and May, 1921.

[41] *Brit. J. Phot.*, 1922, **69**, 110.

[42] *Phot. J.*, 1921, **61**, 425; *J.*, 1922, 36A.

The conclusions regarding the determination of the activity of developing bases[43] indicate that past work in which the depressent action of potassium bromide has been taken as a measure of the activity of a given developing agent may have to be repeated under somewhat different conditions. It appeared that where any given developing solution contained an excess of alkali the addition of small amounts of potassium bromide did not cause a depression of density in the way it does if the alkali is not in excess. It appears therefore that in future work on these lines a preliminary determination of the correct constitution of the developing bath, without bromide, will have to be made for each developer. In addition, Ermen found that most of the developing agents did not require the addition of an alkali to activate them even when the sulphite with which the solution was compounded was neutral to phenolphthalein. Without alkali the images produced were similar in appearance to those obtained by so-called physical development; they were generally cleaner than physically developed images, however, and suggested that "stand" developers giving harmonious negatives eminently suitable for enlarging may be compounded without alkali.

It would be of interest to study with these solutions the action of those dyes which Lüppo-Cramer has found[44] to have an accelerative effect on normally compounded developing solutions. The results might afford evidence in support of R. E. Lisegang's theory.[45] The stabilising of diaminophenol solutions has latterly received much attention,[46] but it cannot be said that any preservative more powerful than glycollic acid, recommended by the writer,[47] has been discovered.

Other items of interest in the year's work on developers and development include a communication by J. I. Crabtree[48] on the photographic examination of developers, one by S. E. Sheppard[49] on an electrochemical study of developers, and a third by E. R. Bullock,[50] which deals with the restraining effect of borax in developing solutions. This last worker shows that the restraining action is due entirely to the reduction of the alkalinity by the added borax. In addition the temperature coefficient in the development of "Dupli-Tized" X-ray film has been determined over a limited temperature range,[51] and it has been shown that the addition of potassium ferrocyanide,[52] once frequently recommended, is without measurable effect.

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[43] *Ibid.*, 1922, **62**, 123. *J.*, 1922, 270A.

[44] *Koll.-Zeits.*, 1922, **30**, 114; *Die Phot.*, 1922, 29; *see also reference* 32.

[45] *Phot. Ind.*, 1922, 601.

[46] L. J. Bunel, *Bull. Soc. franç. Phot.*, 1921, **8**, 290. A. Bunel, *Il Prog. Fot.*, 1921, **28**, 204. L. Lobel, *Bull. Soc. franç. Phot.*, 1921, **8**, 291; *J.*, 1922, 36A.

[47] *Brit. J. Phot.*, 1920, **67**, 642.

[48] *Ibid.*, 1922, **69**, 153, 170, 188,

A. Seyewetz has described the preparation and developing properties of *p*-aminophenolsulphonic acid,[53] whilst the ageing and decomposition of sulphite-quinol solutions has been re-studied by J. Pinnow.[54] Finally the communication of Lüppo-Cramer must be cited,[55] as it indicates that the sensitiveness of any emulsion is a variable depending upon the conditions of development.

The "fixing" of the developed silver image is a matter about which most photographers assume there is nothing new or of importance to be discovered. E. R. Bullock, however,[56] brings new evidence of the mechanism of fixation. For many years it has been assumed that the fixing reaction, *i.e.*, the solution of unchanged silver halide with thiosulphate, ocurrs in two stages, the first being the formation of an insoluble double salt of the formula $Ag_2S_2O_3,Na_2S_2O_3,H_2O$, and the second stage the addition of further thiosulphate forming the readily soluble salt $Ag_2S_2O_3$ $2Na_2S_2O_3$, $2H_2O$. It was the rule to attribute all fixing stains to incomplete fixation, *i.e.*, the production of the insoluble double salt only, and although Lüppo-Cramer has opposed this view and offered satisfactory evidence of other causes of the fixing stains, it has been the standard doctrine of fixation. Bullock now confirms the observations of Lumière and Seyewetz made in 1907 that there is no intermediate stage in the fixation, except in so far as the solution of chloride or bromide before iodide may be considered as such, and that immediately the opalescence disappears from the negative (or positive) fixation is complete. Two communications dealing with the washing of plates etc. have both been preliminaries to applications for patents. K. C. D. Hickman and D. A. Spencer,[57] as the result of a thorough investigation of the various washing devices at present obtainable commercially—an investigation in which plates dyed with Tartrazine were used in lieu of thiosulphate-bearing plates—evolved a most efficient water-pump-cum-siphon device, which is particularly suited to "dish" washing. L. Lumière[58] uses a capillary siphon made by placing a piece of porous material in contact with the surface to be washed and allowing the wash water to act only via this material. Thorough to be with distinct economy of time and wash water are claimed washing effected.

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[49] *Trans. Amer. Electrochem. Soc.*, 1921, **39**; *Chem. Abs.*, 1921, **15**, 2393.
[50] *Brit. J. Phot.*, 1921, **68**, 639; *J.*, 1922, 79A.
[51] *Kodak Abstracts Bull.*, 1922, **8**, 330.
[52] *Ibid.*, 376.
[53] *Comptes rend.*, 1922, **174**, 296; *J.*, 1922, 169A.
[54] *Z. wiss. Phot.*, 1922, **22**, 72; *J.*, 1922, 879A.
[55] *Koll.-Zeits.*, 1921, **29**, 314; *Phot. Ind.*, 1921, 797; *J.*, 1922, **79A**.
[56] *Brit. J. Phot.*, 1922, **69**, 110.
[57] *Phot. J.*, 1922, **62**, 225.

AFTER-TREATMENTS.

The mechanism of the "reduction" with persulphates appears to lose little of its fascination for photographic research workers, and in spite of careful investigation it cannot be contended that an altogether satisfactory theory of the well-known and very valuable super-proportional reduction has been advanced. In fact a perusal of the year's work on this process[59] leaves one with suspended judgment, but somewhat inclined to the belief that the history of the image previous to reduction with persulphate may have a not inconsiderable influence on the type of reduction which will be obtained by any given formula. The controversy which has ranged round this reducer has led us little further than the early ideas of H. Marshall, and it is significant that a worker of the repute of S. E. Sheppard has come to regard a physical, in contra-distinction to a chemical, explanation as the most satisfactory, thus agreeing with Lüppo-Cramer's original theoretical conclusions.

The chemical toning of the silver image has brought little new work forward. S. O. Rawling[60] has attempted to ascertain whether colloidal sulphur *per se* will react with the silver of a bromide print. A slow positive reaction was observed, as also was the case when a solution of hydrogen sulphide free from colloidal sulphur was allowed to remain in contact with a bromide print. He suggests that the toning which occurs in the hypo-alum process or, one presumes, in such a "cold" process as that mentioned in the communication from the Eastern Kodak Research Laboratory,[61] is due to the action of colloidal sulphur formed in the gelatin contiguous to the silver grains and to some extent also to hydrogen sulphide. The toning of silver images with tin compounds is dealt with by F. Formstecher[62] in a communication in which instructions are given for the preparation of reagents giving a variety of tones from violet-black to reddish-sepia. It is pointed out that in each case the toned image, being an adsorption complex of metallic silver and metastannic acid, is very permanent. The same worker has also made two communications dealing with the theory of the toning of printed-out silver images with the noble metals,[63] the latter of which deals fairly exhaustively with palladium toning, and a further communication,[64] in which a process for producing double tones on selenium-toned prints by the application of the Howard Farmer reducer is detailed. The objectionable double tones occasionally encountered on prints toned by the sulphide or copper processes are ascribed by A. R. Riddle[65] to incomplete removal of a double thiosulphate of sodium and silver. It is stated that a five minutes' immersion of the print previous to toning in a 0·6% solution of potassium percarbonate converts this double salt into a soluble tetrathionate which may be completely removed by half an hour's washing.

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[58] *Rev. franç. Phot.*, 1922, **3**, 109.

[59] G. I. Higson, *Chem. Soc. Trans.*, 1921, **119**, 2048. S. E. Sheppard, *Phot. J.*, 1921, **61**, 450. G. I. Higson, *Phot. J.*, 1922, **62**, 98; *J.*, 1922, 234A. S. E. Sheppard, *ibid.*, 381. R. Namias, *Il Prog. Phot.*, 1922, **29**, 161.

[60] *Phot. J.*, 1922, **62**, 3; *J.*, 1922, 80A.

[61] *Report No.* 1360, *Eastman Kodak Research Laboratory.*

[62] *Phot. Rund.*, 1921, 277; *J.*, 1922, 80A.

K. Kieser[66] suggests various toning processes applicable as analytical methods for determining the composition of emulsions and the size of the grain. Although the suggested methods are more or less empirical they are calculated to constitute rapid means of arriving at information of considerable value to the emulsion maker. A mercurial process of producing brown tones on bromide and gaslight prints is described by A. Steigmann,[67] but the well-known fugitive nature of images containing mercury is likely to deter photographers from using the process to any great extent. The tone and permanence of a sulphide-toned image leaves so little to be desired that any quick-acting cold sulphide toning process which may be discovered in the future is certain to be instantly adopted.

PHOTO-MECHANICAL.

The history of the introduction of photographic methods into the printer's domain is not altogether dissimilar to the story of the camel which sought shelter for its nose only, finally ending in complete possession of the owner's tent. From the slightest assistance in minor illustrations rendered in the beginning, its progress has been of so steady and valuable a nature that at the present moment "everything points to the fact that photographic methods will dominate all printing efforts."

The quoted statement was made by one well qualified to express an opinion on the progress in this branch of photography,[68] and, indeed, in general printing circles more than the average amount of attention is being accorded the various photographic processes of type and illustration reproduction, particulars of which have been lately published. Progress of this kind does not strictly appertain to the domain of chemical industry, but as there is every indication that sensitive photographic film will be used in large quantities in the processes now approaching the condition of practical application, there is little need for apology for referring to the matter. Those who are directly interested will find much valuable information in the above referred to Annual—more particularly in the first article therein "A Review of Process Work," by W. Gamble—and in the patent specification which accompanied J. Robertson, T. W. Brown, and A. Orell's application.[69] W. Gamble has also epitomised the present situation in a communication to the Master Printers' Association.[70] Various items of more specific interest have appeared dealing *inter alia* with the subject of the etching of printing surfaces,[71] with the function of the "flash" exposure in three-colour half-tone,[72] with the influence of diffraction when calculating the "screen" separation distance,[73] and with the modification of "blue prints" to render their reproduction on ordinary plates less difficult.[74]

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[63] *Phot. Ind.*, 1921, 874; 1922, 774.

[64] W. Frostmann, *Phot. Rund.*, 1922, **59**, 173.

[65] *Trans. Proc. Roy. Soc., S. Australia*, 1920, **44**, 293.

[66] *Phot. Korr.*, 1922, **59**, 33.

[67] *Phot. Ind.*, 1921, 797.

[68] "Process Year Book," 1923, 54.

The Ullmann process for the production of negatives from opaque—*i.e.*, non-transparent—originals, a process which is an improvement on the old Playertype, and in which the printing is effected through the original whilst this latter is in face to face contact with a bichromated gelatin film, has been improved by prevention of the wandering of the dye used for staining the tanned image. This is effected by the insolublisation of the dye after staining.[75] Any improvements in this process are of interest, for it has been demonstrated to be of particular value in the true-to-scale reproduction of material bound in book form, since it does not entail dismemberment.

RADIOGRAPHY.

Few experimenters with radiographic sensitive material appear to be investigating the radiographic sensitiveness of the different compounds which could be employed in emulsion making, the general bias remaining as hitherto in favour of external intensification appliances. These intensifying screens serve to degrade a portion of the energy of any X-rays falling on them to "light" to which the ordinary photographic emulsion is sensitive. The efficiency factor of this degradation is sufficiently low to allow of marked advantage accruing from the use of two screens, one in contact with either side of duplex coated photographic film. It is also recorded that optical contact of intensifying screen and sensitive surface leads to a further increase of efficiency—patents covering assemblages of this type have been granted to N. E. Luboshez[76]—and it therefore appears probable that the chemical combination of an X-ray degrading substance with a light-sensitive compound would be more efficient than any known or suggested physical combination. Attempts have been made in the past to incorporate the intensifying material in the emulsion, but without much success. Our knowledge of the properties of intensifying compounds has been enlarged since then, however, and further investigation should be worth while. As touching the properties of intensifying screens, it is evident that the non-phosphorescent highly fluorescent alkaline-earth tungstates as prepared by E. Tiede,[77] constitute an improvement likely to be of value more particularly, perhaps, in radiographic kinematography, and also in such a device for stereoscopic "roentgenscopy" as that referred to by J. v. E. Tengbergen.[78]

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[69] E.P. 186,225.

[70] *Brit. J. Phot.*, 1922, **69**, 692.

[71] H. M. Cartwright, *Phot. J.*, 1921, **61**, 428. R. R. Page, *Amer. Prin.*, Jan. 20, 1922, 57. W. J. Mellersh-Jackson, E.P. 176,412 K. Schlecht, U.S.P. 1,414,093.

[72] E. L. Turner and C. D. Hallam, *Phot. J.*, 1922, **62**, 400

[73] E. A. Bierman, *Brit. J. Phot.*, 1922, **69**, 415.

[74] *Report* 998, *Eastman Kodak Research Laboratory.*

[75] M. Ullmann, E.P. 156,691.

With the increase of electrical energy which can be applied in modern X-ray exciting apparatus the influence of scattered radiation, resulting from electronic disturbances in matter of the type discussed by M. de Broglie,[79] has become of vital importance. Any exact study of this scattered radiation is therefore of more than transient interest. R. B. Wilsey[80] has continued his researches in this matter, and his conclusions confirm his previous statements relative to the improvement in radiographic images which is obtainable by the use of the Potter-Bucky diaphragm, a description of which has been given by C. H. Holbeach.[81] A patent for a modified diaphragm in which two opaque eccentric discs, pierced with holes in such a way that they are in constant alinement with the target and which make one revolution per exposure, obtained by A. Dauvillier,[82] constitutes further evidence of the technical importance of such apparatus. Attention to details of the photographic technique of radiography in conjunction with the duplex-coated, *e.g.*, "Dupli-Tized" film, has led to enormous strides in the production of images relatively free from contamination by secondary images due to scattered radiation. It will be clear that by pushing the use of intensifying screens to the limit and subsequently procuring the necessary opacity by the super-imposition of two relatively weak (short-developed) images in which the secondary scattered images have not been developed, improved results were to be expected. Not only does the use of screens allow of the shortening of exposure, with a corresponding gain in definition owing to diminution of movement risk, but also for any given exposure it allows of reduction of the tube voltage with corresponding decrease in the relative proportion of scattered radiation.

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[76] E.P. 181,087, 182,496 and 184,519.
[77] G.P. 353,057; *J.*, 1922, 729A.
[78] *Arch. Radiol.*, 1921, **26**, 42.
[79] *J. Phys.*, 1921, **2**, 265.
[80] *Amer. J Roent.*, 1921, **8**, 589.
[81] *J. Roent. Soc.*, 1921, **17**, 179.
[82] F.P. 521,746.

A further communication of interest in screen technique in that it affords striking evidence of the relative insensitiveness of the photographic emulsion to X-rays is that of A. Zimmern,[83] in which it is pointed out that although increase of the temperature of the emulsion from the normal to 60° C. practically halved the exposure necessary for any given density of developed image, no thermal intensifying effect was noticed when intensifying screens were employed. The influence of temperature on the sensitiveness of photographic emulsions to X-rays will no doubt receive further attention; it is difficult to understand, more particularly since Lüppo-Cramer has shown that desensitisers effective in the visible spectrum are also effective in the X-ray spectrum.[84]

THEORETICAL.

A most interesting discussion has been started by the publication of F. Weigert and W. Scholler's work[85] which has led these experimenters to the conclusion that the light-sensitive substance in a P.O.P. emulsion is not the silver chloride but the other (soluble) silver salts. In the case of pure halide emulsions, it is suggested that the light-sensitive material is really metallic silver, which is present in minute quantities as an impurity.

The former worker[86] has also verified the Einstein photochemical equivalent law in the case of P.O.P. emulsions, for the earliest stages of exposure, making the assumption that the light is absorbed by silver only, and not by silver+silver chloride.

Although Lüppo-Cramer[87] maintains that Weigert's results support the generally accepted view of the continuous decomposition and regeneration of silver chloride during the exposure of an emulsion containing chloride and a soluble silver salt, and although, further, it has been shown that halogen is liberated in weighable amounts from the halides of silver when exposed for long periods,[88] it would be of interest to repeat the work above referred to on pure unripened halide emulsions made from silver salts, which have been prepared from the metal in the absence of actinic light, and also on pure halide emulsions which have been desensitised to the greatest possible extent. This latter expedient (desensitisation) should provide material for an investigation, which might lead to some valuable conclusions as to the relative merits of the silver nucleus sensitivity theory of Lüppo-Cramer—latterly supported experimentally by W. Clark[89] and mathematically by F. C. Toy[90]—and the light quantum theory propounded by L. Silberstein[91] and further investigated experimentally by A. P. H. Trivelli and F. L. Righter.[92]

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[83] *Comptes rend.*, 1922, **174**, 453; *J.*, 1922, 233A.

[84] *Phot. Ind.*, 1922, 287.

[85] *Sitzungsber. Kgl. Preuss. Akad. Wiss. Berlin*, 1922, 641 *J.*, 1922, 120A; *Physik. Zeits.*, 1921, **22**, 674.

[86] *Loc. cit.*

[87] *Phot. Ind.*, 1921, 1029.

Until an emulsion is prepared which is admittedly free from nuclei or reduction centres whilst being in all other respects physically identical with an emulsion bearing nuclei, it would appear to be almost impossible to conduct any research which might elucidate either the nature of light or the influence of nuclei.[93] Ripening of a relatively insensitive emulsion usually induces alterations of physical condition which in themselves may have enormous influences on the result. In the reverse process—that of desensitisation—no such physical alterations are introduced; thus it may happen that the process of desensitisation may be of as great import theoretically as it is of assistance in practical photography.

Another aspect of the theory of photography about which opinion is very much divided is that of the effect of contiguity of unexposed halide grains to exposed grains. T. Svedberg[94] has shown conclusively that in the case of an emulsion containing approximately equal sized spherical grains, reducibility is not transferred from one grain to contiguous grains. On the other hand A. P. H. Trivelli, F. L. Righter, and S. E. Sheppard[95] have found experimentally that in the case of flat grains which are "clumped" together the entire group is developable by virtue of one of the grains having been rendered reducible by light action. Their own interpretation of the results of these last workers is questioned by F. C. Toy,[96] who maintains that they are not sufficiently in accord with the theoretical results deduced by Silberstein from his basic assumption of the "quantum" nature of light to be acceptable as evidence in support thereof.

[88] F. Schrader, *Z. Phys.*, 1921, **6**, 127. E. J. Hartung, *Chem. Soc. Trans.*, 1922, **121**, 682; *J.*, 1922, 440A.

[89] *Brit. J. Phot.*, 1922, **69**, 462; *J.*, 1922, 689A.

[90] *Phil. Mag.*, 1922, **44**, 352.

[91] *Ibid.*, 257.

[92] *Ibid.*, 252.

[93] *Cf.* F. C. Toy, *Phot. J.*, 1921, **61**, 417; *J.*, 1922, 36A.

[94] *Phot. J.*, 1922, **62**, 183.

[95] *Ibid.*, 407; *J.*, 1922, 788A.

[96] *Brit. J. Phot.*, 1922, **69**, 443.

At present, therefore, it is clear that the available evidence is not sufficient to warrant conclusions being drawn from photographic experiments, either as to the nature of light or as to the constitution of the sensitive grain. Much work is being carried on bearing upon the physical properties of gelatin—more particularly upon the relation of the hydrogen ion concentration to the properties such as viscosity, swelling, etc.—a useful *resumé* of our present knowledge appearing in a communication by S. E. Sheppard,[97] who states, *inter alia*, that the chemical deportment of gelatin is relatively of little importance in photographic emulsion making, provided impurities are reduced to a minimum. Whilst the importance of the physical properties of gelatin is admitted by most photochemists, there are others who have not yet been convinced that the reducing properties of the colloid used in making the emulsion are of minor importance. Little or nothing appears to have been done in the investigation of emulsions made with chemically modified gelatins—an omission which is the more surprising in view of the fact that for years it has been known that the presence of readily reducible compounds, *e.g.*, the brown manganese compound produced in the reversal stage of the "autochrome" process, markedly reduces the sensitiveness of any given emulsion and their removal (by treatment with bisulphite, for instance) causes resensitisation.

It cannot be dismissed as impossible that in ripened emulsions at any rate the grain is a crystal, the alternate halide molecules of which, or even perhaps the neighbouring atoms of which, are separated by an exceedingly thin film of gelatin. It is asserted by G. Grube and V. Reuss[98] that copper deposited electrolytically from solutions containing gelatin consists of alternate layers of metal and gelatin, and if one were allowed to postulate a similar grain structure in which an oxidisible colloid is in atomic distance relation to an oxidising silver compound, an explanation of the increase of sensitivity by ripening based upon the observations of E. C. C. Baly and his co-workers could be offered. On the same hypothesis a "strain" theory could be built up, for crystals so constituted would, as formed, exist in a state of strain, would therefore exhibit selective absorption towards polarised light[99] and would suffer internal disruption by electronic breaking of the oriented dielectric gelatin wall separating the light-sensitive constituents.

The marked affinity for small amounts of the gaseous halogens which gelatin exhibits would become of vital importance both in the ripening and exposure state of emulsion operations and the phenomena of reversal, which occurs, so far as the writer's experience goes, only when emulsions loaded with free halogen are developed in the absence of actinic light, would be readily comprehensible. The action of desensitisers as saturators of the affinity of the gelatin for halogen is not contrary to such a conception, while the rôle of sensitisers would be strictly analogous to that of the dyes used in Baly's experiments and the importance of the chemical constitution of such dyes becomes apparent.

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[97] *Ibid.*, 677, 695, 710; *see also* T. S. Price, *Phot. J.*, 1922, **62**, 356.

[98] *Z. Elektrochem.*, 1921, 45.

[99] F. Weigert, *Ann. Physik*, 1920, **63**, 681. J. W. Woodrow, *J. Amer. Phys. Soc.*; *Brit. J. Phot.*, 1922, **69**, 232.

Whatever theory is provisionally accepted as a working hypothesis, however, will have to explain a multitude of phenomena, many of which appear to be of a purely physical character and in some cases are conditioned solely by concentration factors. Thus it must be able to clear up satisfactorily such an anomaly as is referred to by Lüppo-Cramer,[100] *i.e.*, a 1:20,000 solution of Phenosafranine causes light to destroy effectively the latent image embedded in silver iodide, whilst a 1:2000 solution is without action; further, the desensitising powers of such solutions are, in the case of iodide, an inverse function of the concentration, whilst, in the case of bromide, they are a direct function thereof. It would be of interest to know whether any similar variations occur in the destruction of the latent image by light in the Freund desensitisation process as modified by F. F. Renwick.[101] Fortunately the photographic industry is not dependent for its progress upon the theoretical explanation of many of its most interesting and useful phenomena and, much as the scientific investigator who interests himself in this subject deplores the present unsatisfactory condition of theory, he cannot but realise that even if photography has to be regarded as the outcome of haphazard rule-of-thumb experimentation, it is proving itself of inestimable value in the sciences and playing a most important rôle in the instruction, amusement, and ennoblement of all civilised communities. When its products can be produced with the regularity and certainty which characterise other chemical industries operated on well-established and generally accepted theories, enormous expansion in its application may be safely prophesied.

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[100] *Phot. Ind.*, 1922, 195.

[101] *J.*, 1920, 156T.

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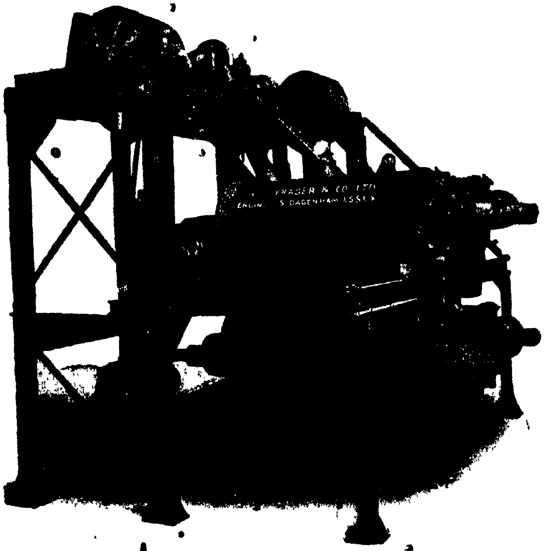

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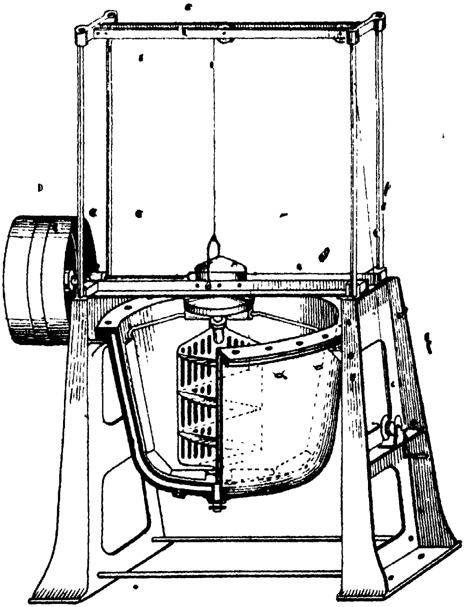

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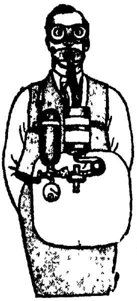

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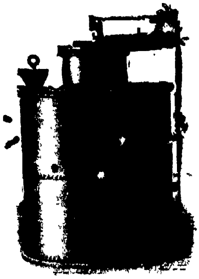

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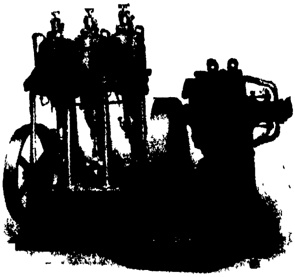

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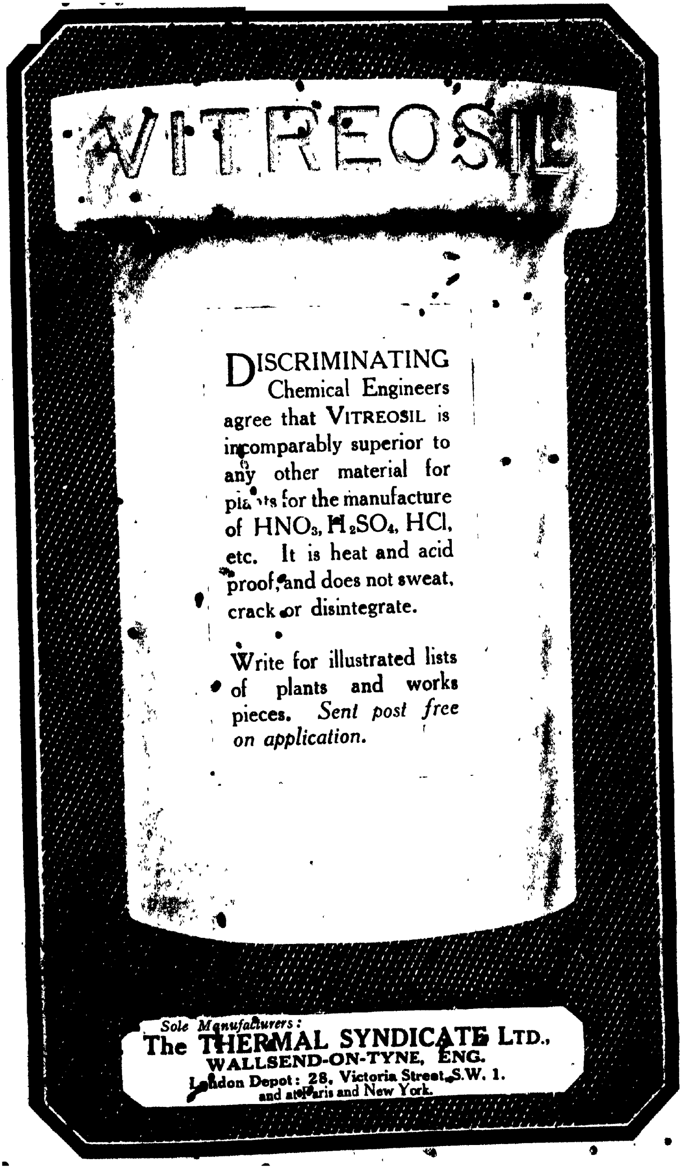

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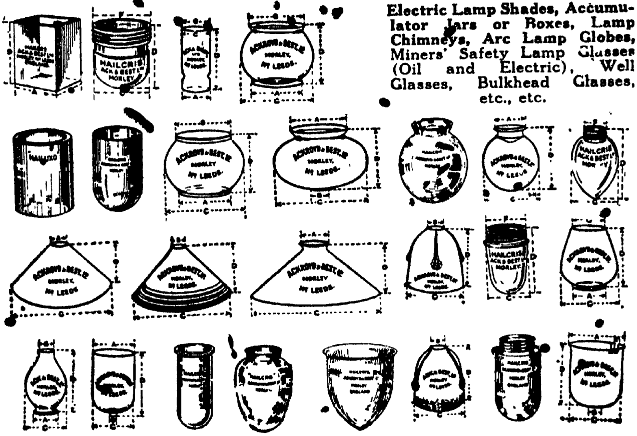

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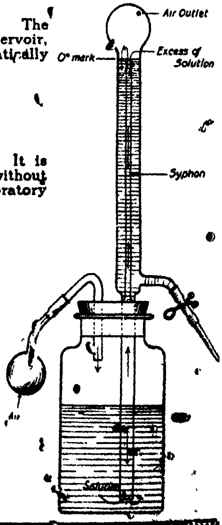

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